Energetics and Power Generation

Klaus Schadow
Schadow Technology
2896 Calle Heraldo
San Clemente, CA 92673

E-mail: schadowkc@cox.net

Materials that are produced on the nanoscale have the promise for increased performance for energetics (such as propellants & explosives) and power generation devices (such as batteries & fuel cells and hydrogen storage).

1. Energetics

For solid propellants, nanomaterials promise increased energy density, controlled energy release, reduced sensitivity, reduced environmental impact, and long-term stability (Ref. 1 and 2). In the near-term novel propellants with nanoscale material will be used to reduce particle size dispersion (greater uniformity), reduce agglomeration of aluminum (increased combustion efficiency), and increase reaction rates (increased burning rates). In the long-term radical new propellant approaches will be explored to utilize 3-dimensional nanostructures that might yield controllable energy release and tailorable sensitivity.

Novel nanostructured propellants have the potential to combine the advantages of conventional composite and monomolecular propellants (Ref. 3). In conventional propellant composites, oxidizer and fuel are mixed to obtain desired energy properties. However, due to the granular nature the reaction kinetics are slow, as they are controlled by thermal and mass transport between micron and millimeter-sized particles. In monomolecular materials, where the energy release is controlled by chemical kinetics and not by mass transfer, much higher burning rates and greater power can be achieved than composites. The total energy density of monomolecular materials is only half of that achievable with composites. Based on nanotechnology it may be possible to combine the advantages of monomolecular materials (high burning rates) and conventional composites (tailoring of properties and high energy density).

1.1. Propellants with Nano-Aluminum

Recent experiments have shown that the ignition sensitivity and burning rate of nano-aluminum particles can be significantly higher than micron-aluminum particles. This resulted in increased burning rates and improved combustion efficiency for conventional composite propellants (Ref. 4). It was also observed that the nano-aluminum powder significantly reduced aluminum agglomeration. The low agglomeration rate may be the result of a thin aluminum oxide layer on the aluminum particles as observed on transmission electron microscope images.

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1.2. Nanostructured Propellants

For this new class of propellants, nanostructured pyrotechnics (thermites) and organic nanocomposites (propellants) will discussed.

For thermites, a method will be described for the synthesis of nanostructured fuel/oxidizer material (Ref. 5). Fuel and oxidizer association is enhanced by electrostatic forces, which exist between charged aerosols particles. The goal is to enhance interaction of fuel and oxidizer and minimize fuel-fuel and oxidizer-oxidizer interactions by oppositely charging each component in the aerosol. The nanoscale assembly strongly depends on the collision rate between fuel and oxidizer particles. For the specific example with an aluminum/iron oxide thermite mixture, the flame propagating velocity in a spark ignited sample was significantly increased, when the structures were ordered through bipolar coagulation as compared to random structures with Brownian coagulation. The improvement was also shown with differential scanning calirometry (DSC) analysis. The DSC shows that the rate of exotherm observed in the electrostatically enhanced case is a factor of 10 faster. Transmission and scanning electron microscope studies also showed that the nanocomposites had markedly different energy release and thermal properties compared to conventional micron sized iron oxide thermite, because of the efficient degree of mixing and intimate nanostructuring of the novel material.

For organic nanocomposites, monolithic energetic polymer gels were prepared in acetone by separately cross-linking various precursors (Ref. 6). The synthesis conditions were optimized according to precursor mass ratio, cross-linking agent, solvent, and catalyst concentration to achieve micron and submicron pores. The high energy explosive was trapped in the energetic polymer gel using sol gel processing with a modified freeze-drying process. The compositions of the composite energetic materials were tailored and optimized at the nanoscale according to the desired performance and reduced sensitivity. The impact sensitivity of the composite energetic materials was lower than the pure energetic explosive. With regard to safety the following observations can be made: (1) sol-gel methodology offers advantages in processing with water-like viscocity for casting, ambient temperature gelation, and low temperature drying and (2) decreased sensitivity has been generally observed by shrinking particle size in propellants (because of more homogeneous mixture and fewer potential hot spots). However safety properties need careful evaluation for each new propellant.

Future goals are 3-dimesional nano-energetics with a high degree of structure and order for controlled reactivity and improved manufacturability.

2. Power Generation and Hydrogen Storage

2.1. Batteries and Fuel Cells

For batteries, nanostructured materials are being explored to increase electrical capacity of the electrodes and to increase ion conductivity and long-term stability of the electrolytes (Ref. 7). For lithium batteries anodes, templated nanostructures are being explored to fabricate nanoscale materials having the specific sizes and dimension needed for optimum performance. One example is an anode consisting of 110-nm-diamter SnO_2 nanofibers reduced to a Sn based nanocomposite to increase number of discharge cycles, improve discharge rates, and reduce capacity losses.

For fuel cells, nanostructures are also being explored for electrocatalysts. One example is a nano-architectured Pt catalyst using sol-gel techniques. In this nanomaterial, carbon powder provides a continuous electronic network to the 2-nm carbon-supported colloidal Pt nanoparticles within the continuous nanoscale network of the SiO_2 aerogel. This 3-D porous pathway results in significantly enhanced catalytic activity.

2.2. Hydrogen Storage

For hydrogen storage there are many conflicting reports on the degree of hydrogen adsorption and desorption in nanocarbons (Ref. 8 and 9). Results of around 4 wt% storage in Single Wall Nanotubes (SWNT) and Graphite Nano Fibres have been recently achieved in reproducible tests, which is still below the US Department of Energy goal of 6.5 wt%. Hydrogen storage is also explored in nanostructured magnesium-related materials, which are manufactured through mechanical alloying and milling. These nanomaterials show acceptable hydrogen storage performance at elevated working temperatures, however the storage capacity drops down dramatically at temperatures below 200C. In these tests, hydrogen was essentially loaded under pressure into the nanotubes and nanomaterials (physical approach). In the following hydrogen storage using the chemical approach is discussed.

Single wall carbon nanotubes were electromechanically functionalized with hydrogen and nitro groups (Ref. 10 and 11). Hydrogen adsorption on the SWNTs was carried out in the presence or absence of electrodeposited catalytic nanoparticles of magnesium. For the electrochemical functionalization process, SWNTs were deposited on Teflon-coated membranes by vacuum filtration, lifted off as free-standing nanopaper, and used as the electrodes. Hydrogen uptake on the nanotubes was characterized by micro-Raman spectroscopy, thermogravimetric and thermopower measurements. Adsorbed hydrogen levels up to about 2 weight percent has been observed without catalyst. Mg coating enhanced the hydrogen uptake.

In summary, nanomaterials have a high potential for energetics and power generations. Groundbreaking work has been started and has resulted in first successes. However, science at the nanoscale has to advance to fully exploit the potential of this emerging technology and to understand, control, and fabricate complex nanomaterial structures.

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2) A.W. Miziolek, "Nanoenergetics: An Emerging Technology Area of National Importance", The AMPTIAC Newsletter, Volume 6, Number 1

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ENERGETICS AND POWER GENERATION

Klaus Schadow
E-mail: schadowkc@cox.net

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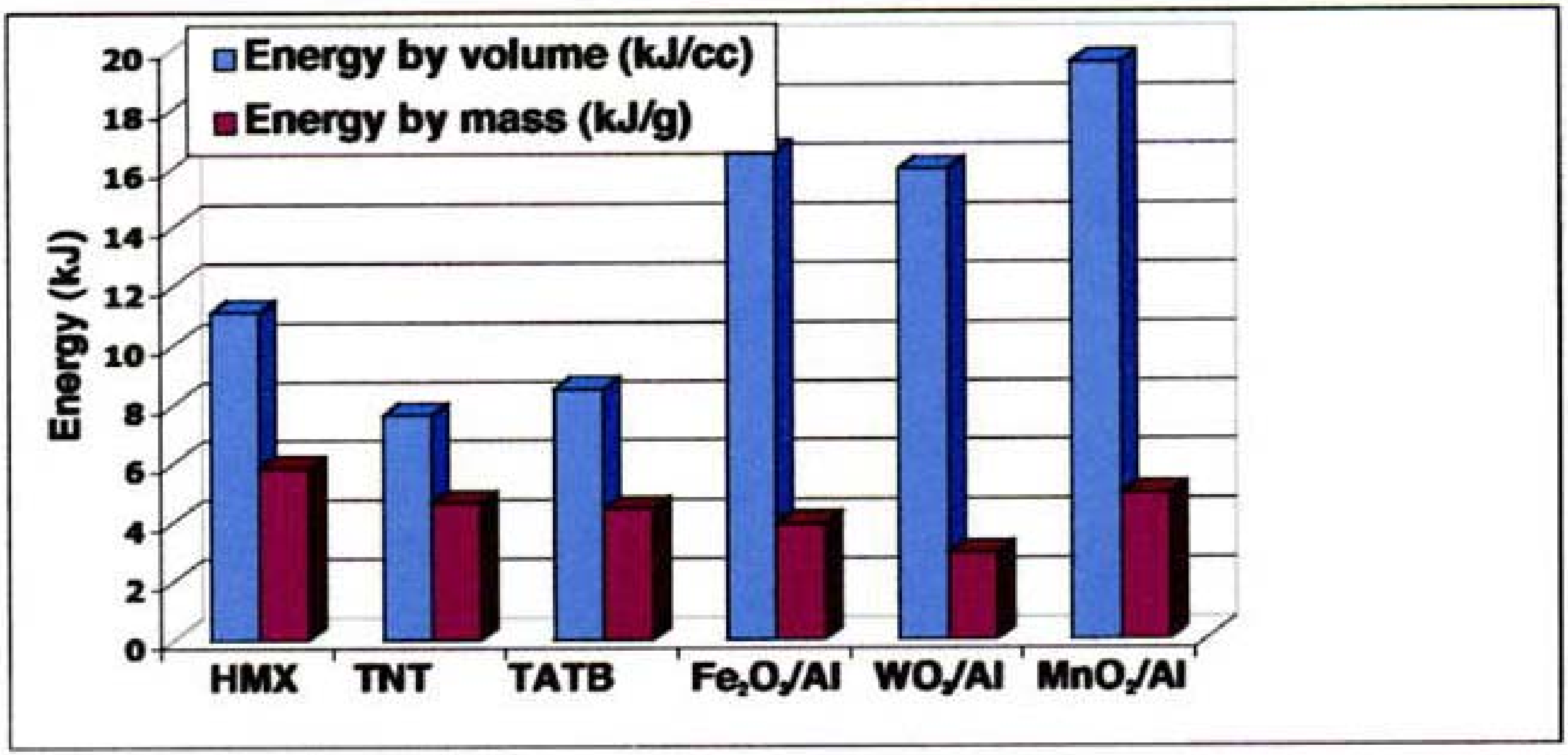
OUTLINE

- ENERGETICS
  - **SOLID PROPELLANTS**
  - EXPLOSIVES
- POWER GENERATION
  - **BATTERIES / FUEL CELLS**
    - NANOMATRIALS
- HYDROGEN STORAGE
  - **CARBON NANOTUBES**
  - **NANOSTRUCTURED Mg RELATED MATERIALS**
  - **FUNCTIONALIZED CARBON NANOTUBES**

Energy and Energy Density Values for Monomolecular and Composite Materials



Monomolecular Material: high regression rate, low energy density

Composite Material: low regression rate, high energy density

Gash, LLNL

Conventional vs. Nanoscale Propellants

Combustion Characteristics of Conventional Propellants Governed by Characteristics of Composite Formulations:

- > **Multi-scale, Multi-component: Particulates plus binder**
- > **Particulate size distributions lead to local non-uniformity and clustering of smaller components**
- > **Significant agglomeration of aluminum (if present) prior to ignition**
- > **Rate of Reaction limited by mass and thermal transport**

A Novel Approach to Propellants Utilizing Nanoscale Materials Might Yield:

- > **Higher reaction rates**
- > **Reduced size dispersion**
- > **Greater uniformity**
- > **Reduce agglomeration of aluminum**

A Radical Approach to Propellants Utilizing 3-Dimensional Nanostructures Might Yield:

- > **Controllable energy release**
- > **Tailorable sensitivity**

MANN, ARO

Approaches to Nanoenergetics

1st Generation (pre 2000)

- Nanometer-sized Al powder/conventional propellants
  - Some performance gain

2nd Generation (current efforts)

- Metal oxide / Al sol-gel quasi-structured nanocomposites (thermites)
- Organic sol-gel quasi-structured nanocomposites (propellants)

3rd Generation (future)

- 3-dimensional nanoenergetics
  - Structured/ordered
  - Controlled reactivity
  - Improved manufacturability/processing

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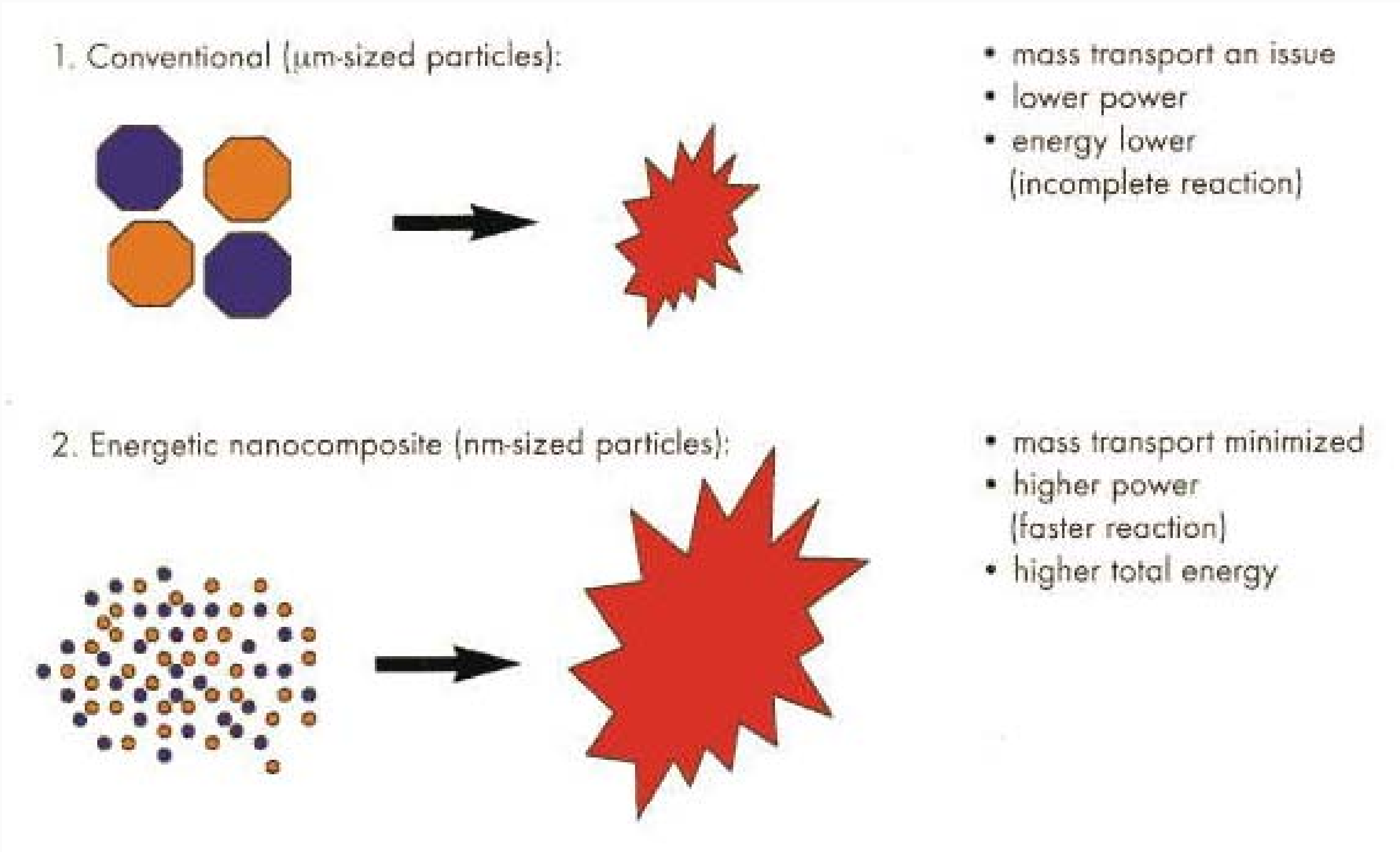
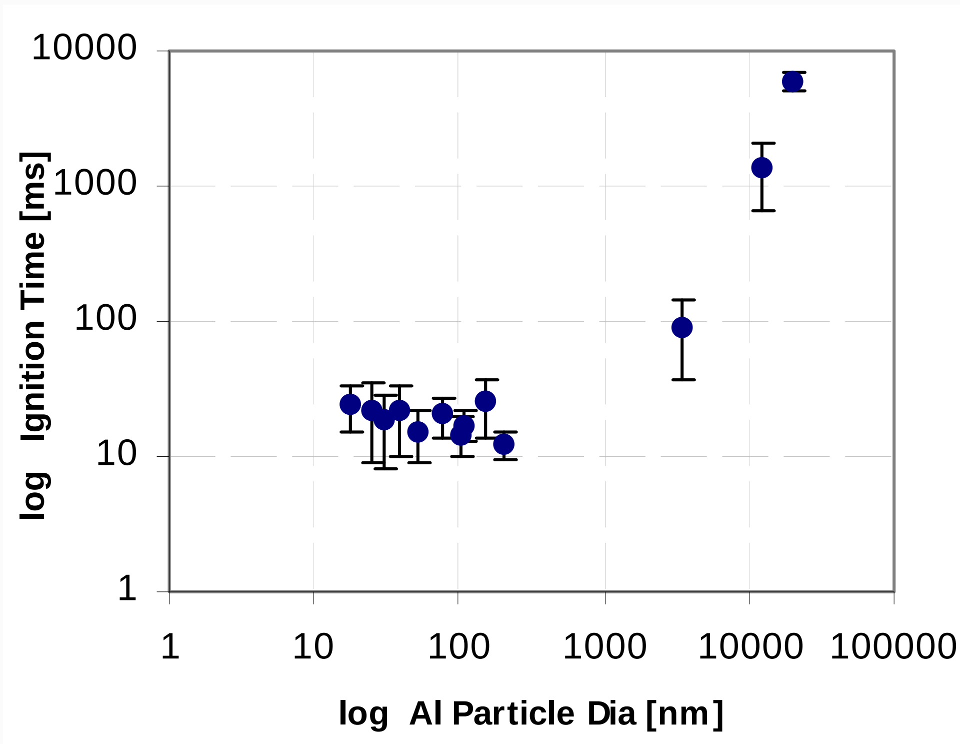
COMPOSITE ENERGETIC MATRIALS CONVENTIONAL VS NANOSIZED



MIZIOLEK, ARL

Propagation Physics and Ignition of Nano-Al Based Energetic Composites - M. Pantoya

Ignition sensitivity of $Al+MoO_3$ pellets: Nano vs. Micron Al



- **Nano-Al reduces time to ignition in Al/MoO_3 by a factor of 100 to 1000.**

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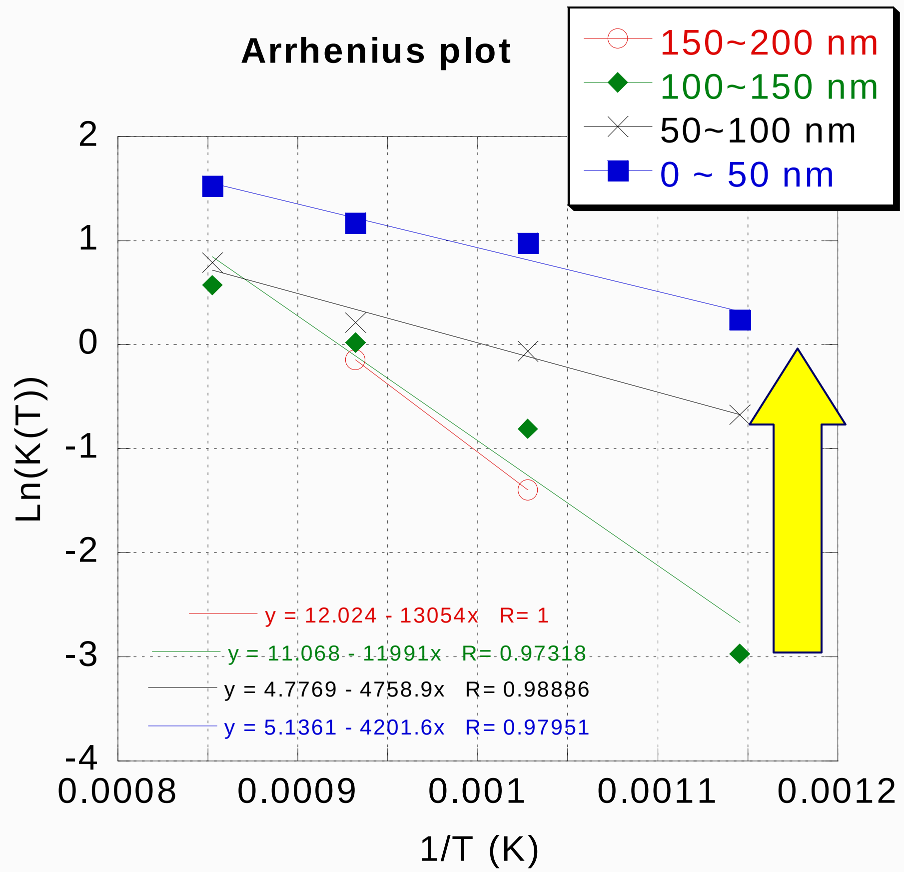
Size-dependent oxidation of Al nanoparticles

Particle produced in DC Plasma Discharge



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Aluminium Nanoparticles in Composite Propellants

Objective:

To study the effect of aluminum particle size ranging from 60 to 0.18 μm on burning rates, processability, and combustion efficiency of PCP/Al/AP propellants.

Propellant Formulation

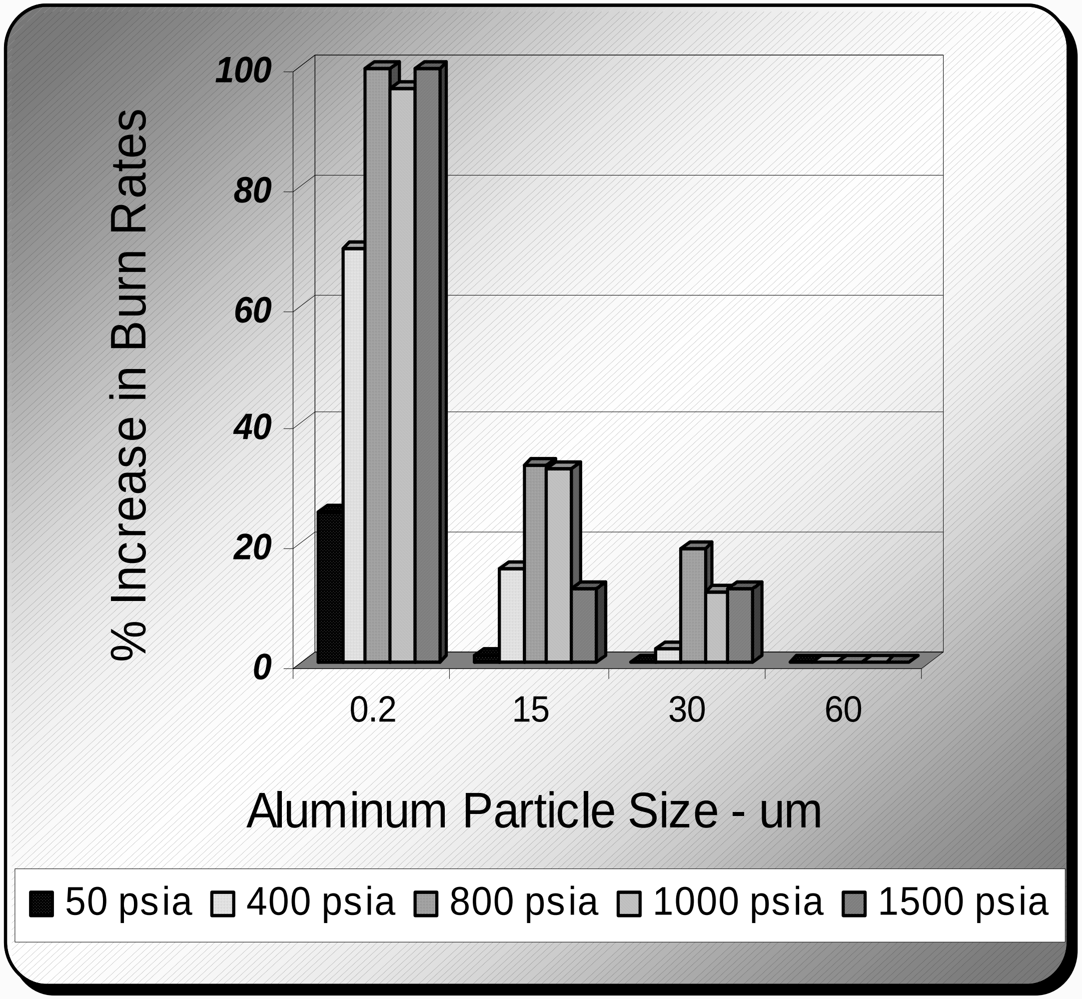
Materials	% Mass
Binder	4.7
Plasticizers	17.3
Aluminum	20.0
AP	57.0
Curing Agents	1.0
TOTAL	100.0

BUI, NAWC

Variables

Aluminum	Particle Size (μm)
H60	60
H30	30
H15	15
ALEX®	0.180

Burning Rate Increase



BUI, NAWC

Burning Samples

50 psia nitrogen

20 % H60

20 % H30

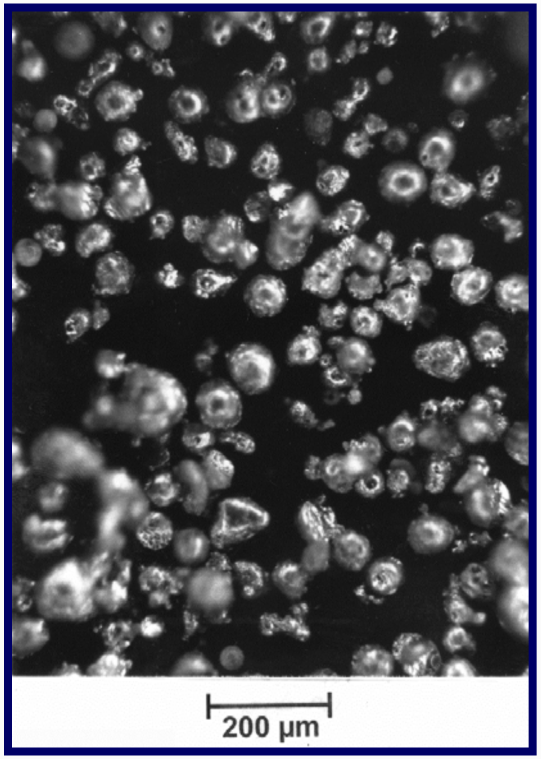
20 % H15

20 % ALEX

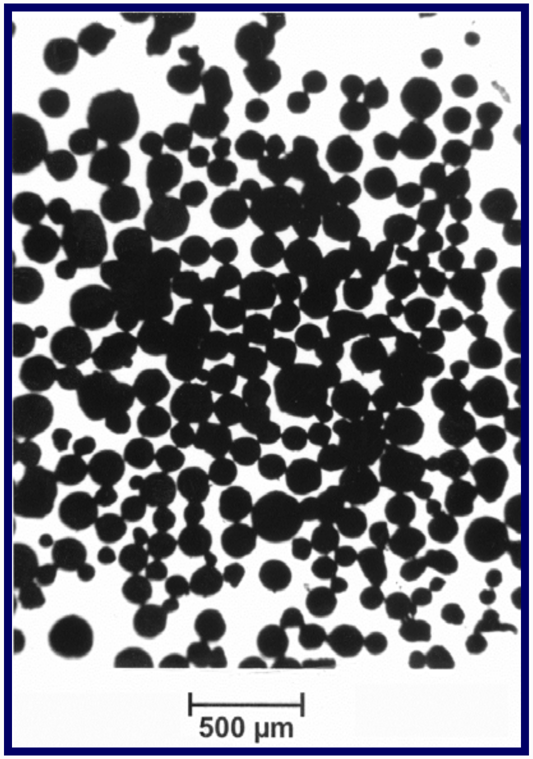
BUI, NAWC

Agglomerates
50 psia nitrogen

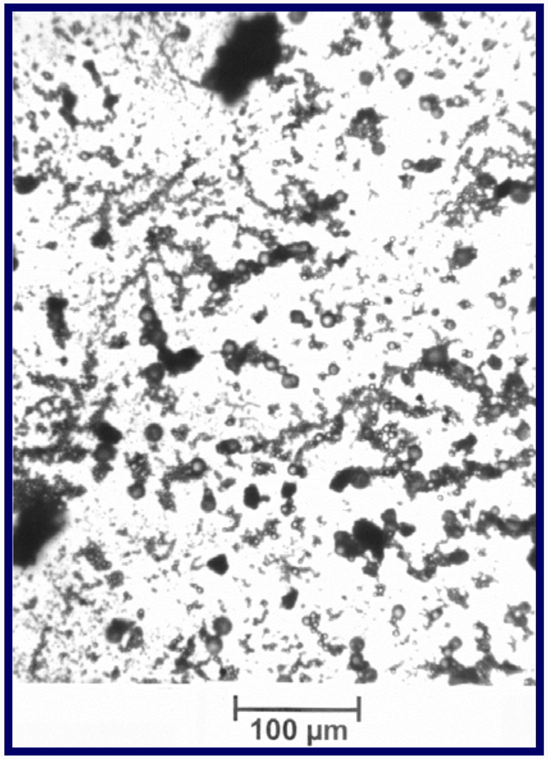
20 % H-60



20 % H-15

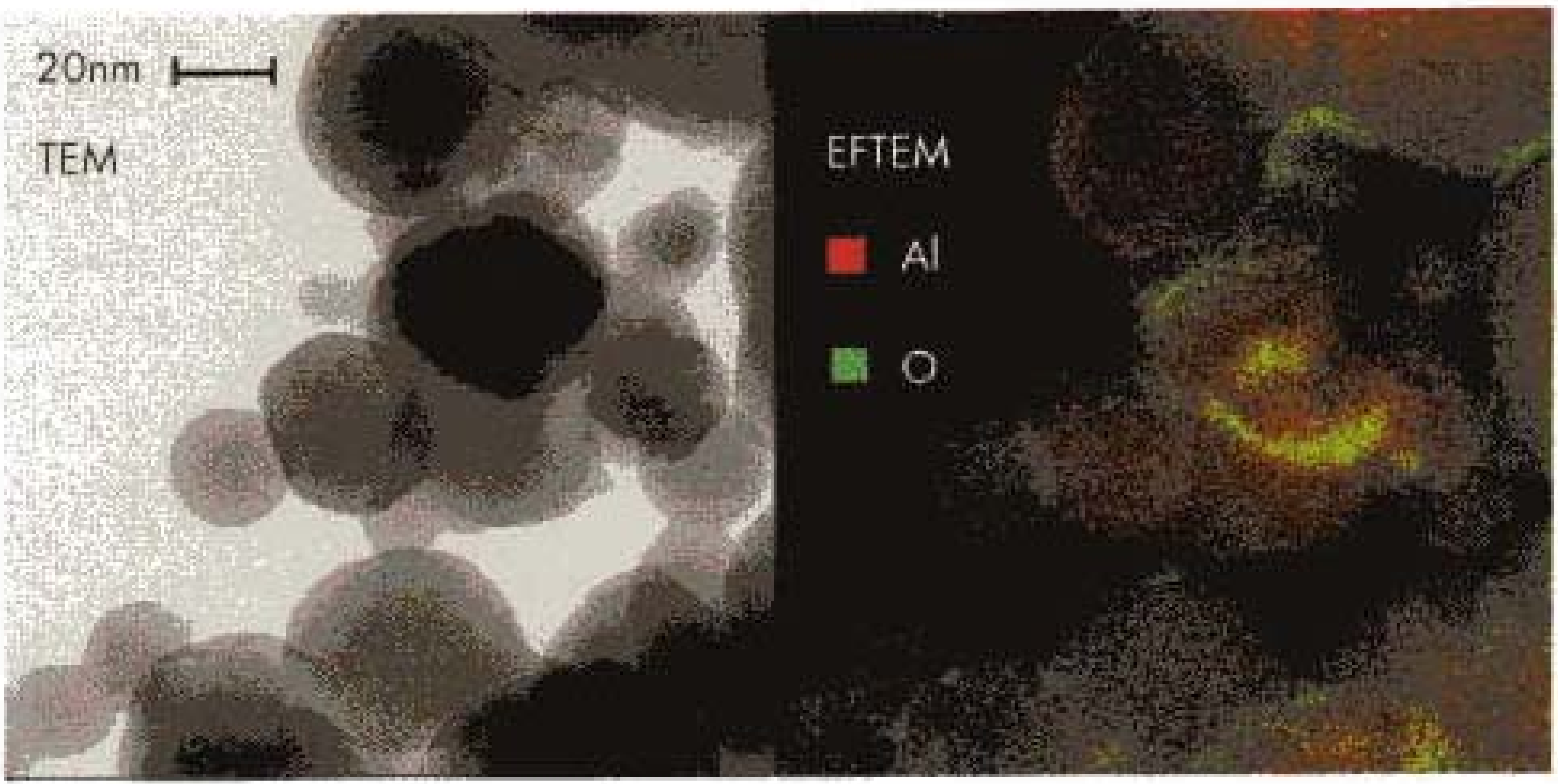


20 % ALEX



BUI, NAWC

Al NANOPARTICLES WITH A PASSIVATION LAYER OF ALUMINUM OXIDE (LLNL)



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Conventional vs. Nanostructured Propellants

Conventional Propellants

Prepared through mixing
Particulates (oxidizer and aluminum) plus binder
Agglomeration of aluminum prior to ignition
Rate of reaction limited by mass and heat transfer
Some success with nanosized aluminum

Nanosstructured Propellants

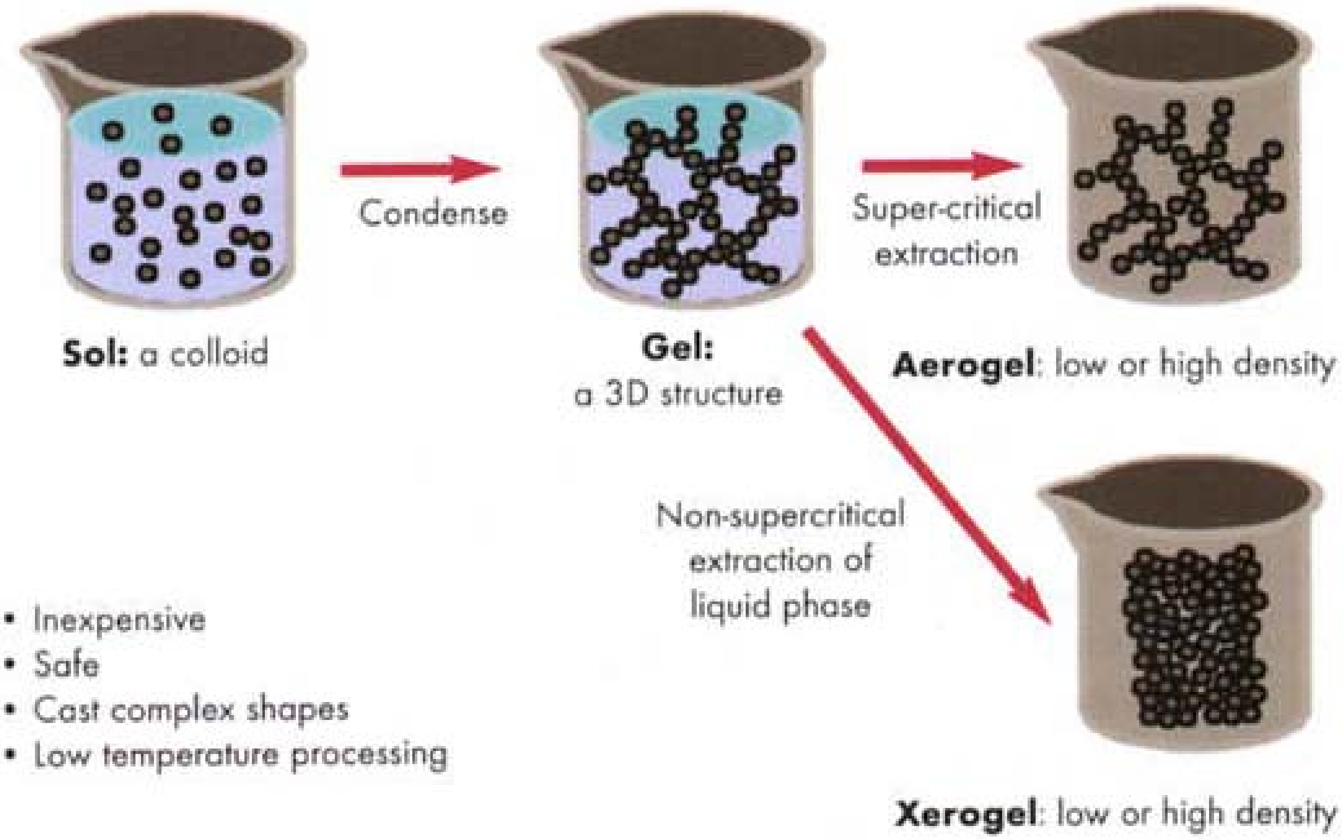
Prepared by sol-gel methodology
High degree of mixing
Greater uniformity
Reduce agglomeration of aluminum
Higher reaction rates

Approaches to Nanoenergetics

2nd Generation (current efforts)

- Metal oxide / Al sol-gel nanocomposites
    - Pyrotechnics (thermites)
    - High heat and light release
- Organic sol-gel nanocomposites
    - Propellants (explosives)
    - High heat and gas release

SOL-GEL METHODOLOGY



- Inexpensive
- Safe
- Cast complex shapes
- Low temperature processing

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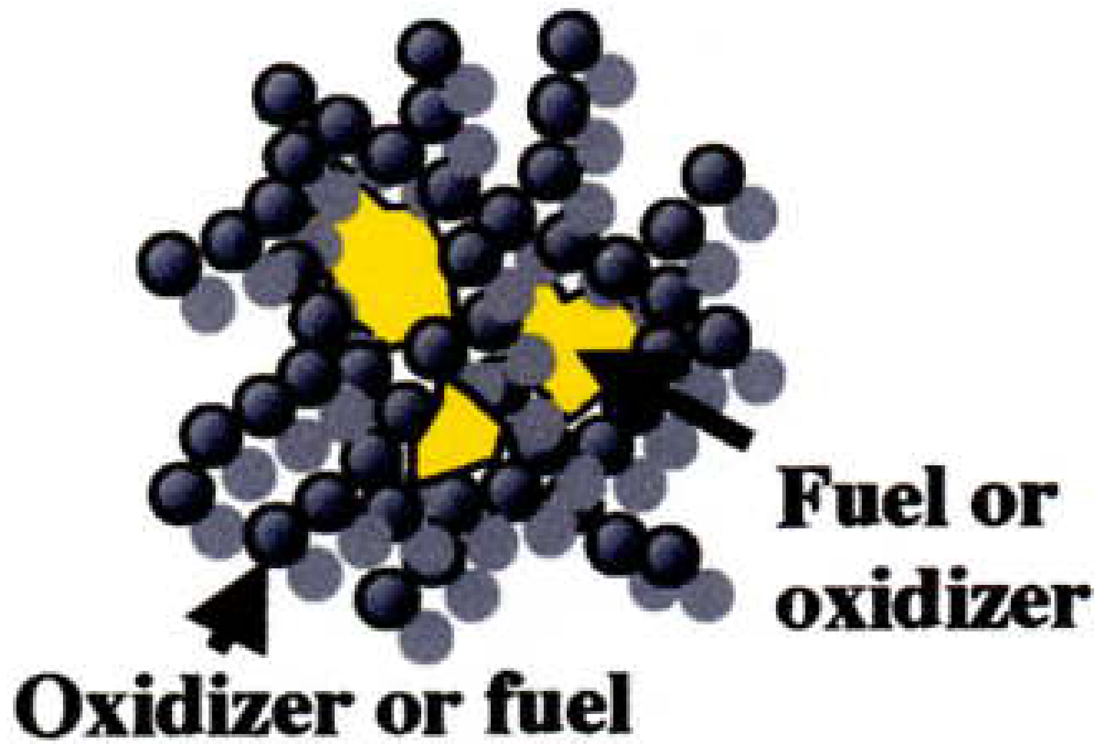
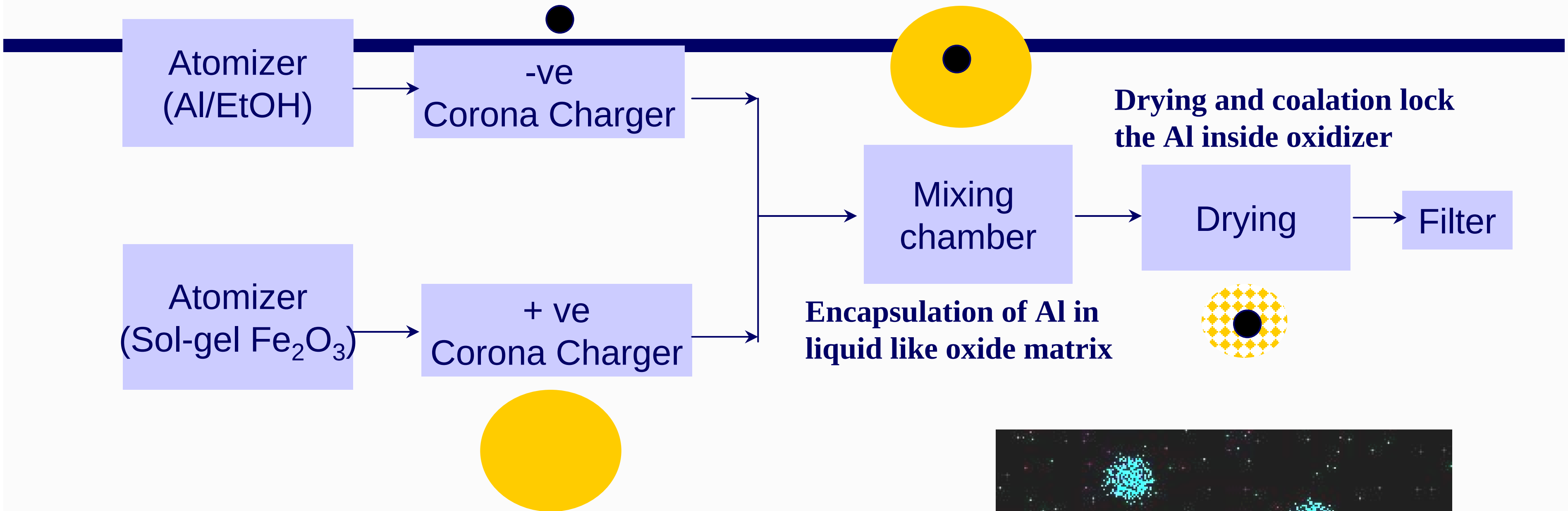
Idealized Sol-Gel Nanostructured Energetic Material



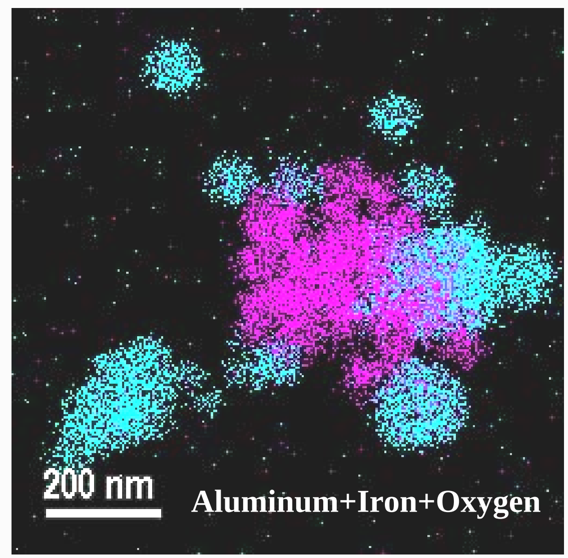
Gash, LLNL

Encapsulation of Al in Fe_2O_3 matrix

DURINT - M. Zachariah, U. Maryland



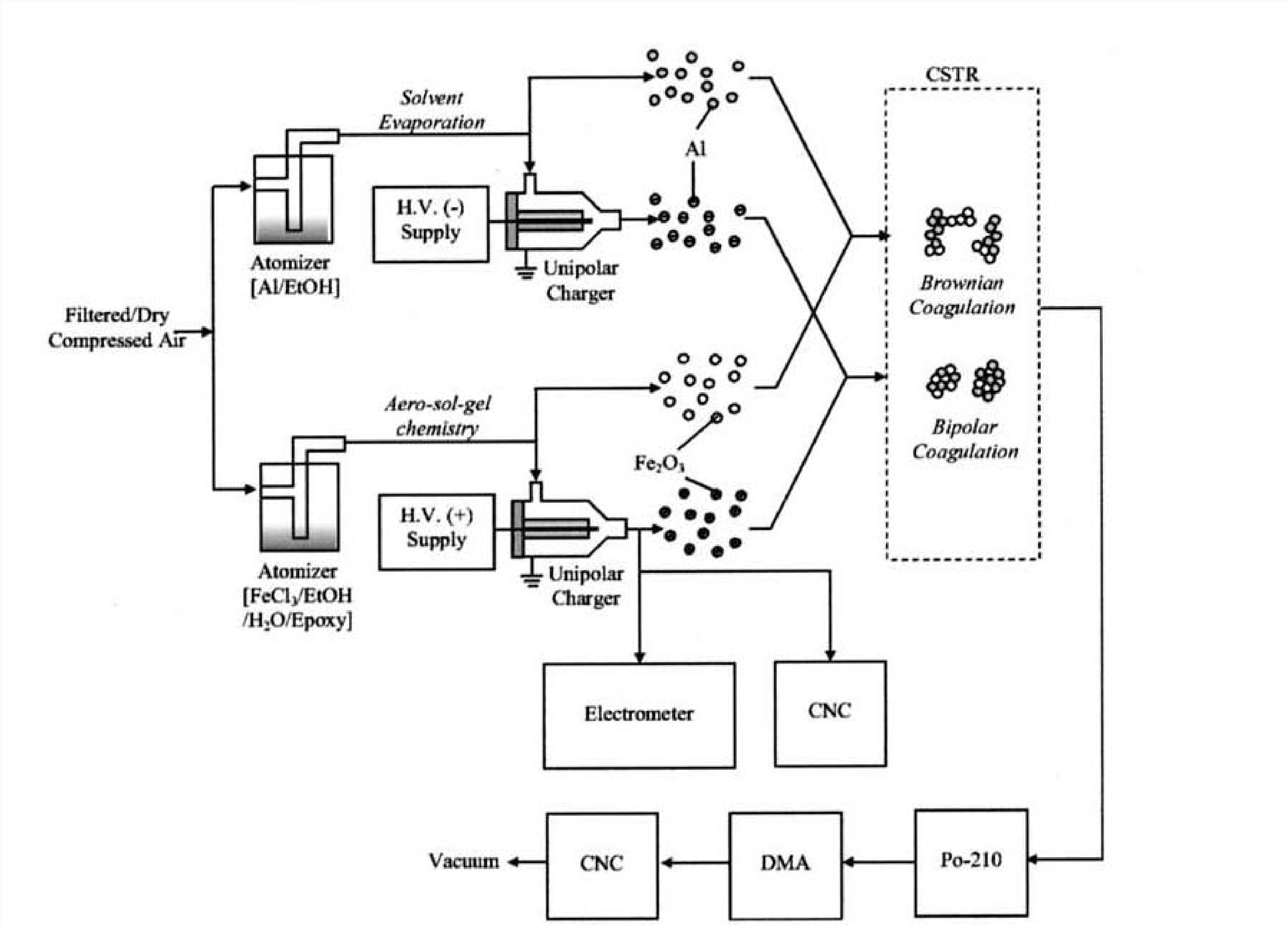
Aerosol - plus - Sol Gel Chemistry for creation of novel Nanostructures



STEM elemental map of coagulated nanoparticle

MANN, ARO

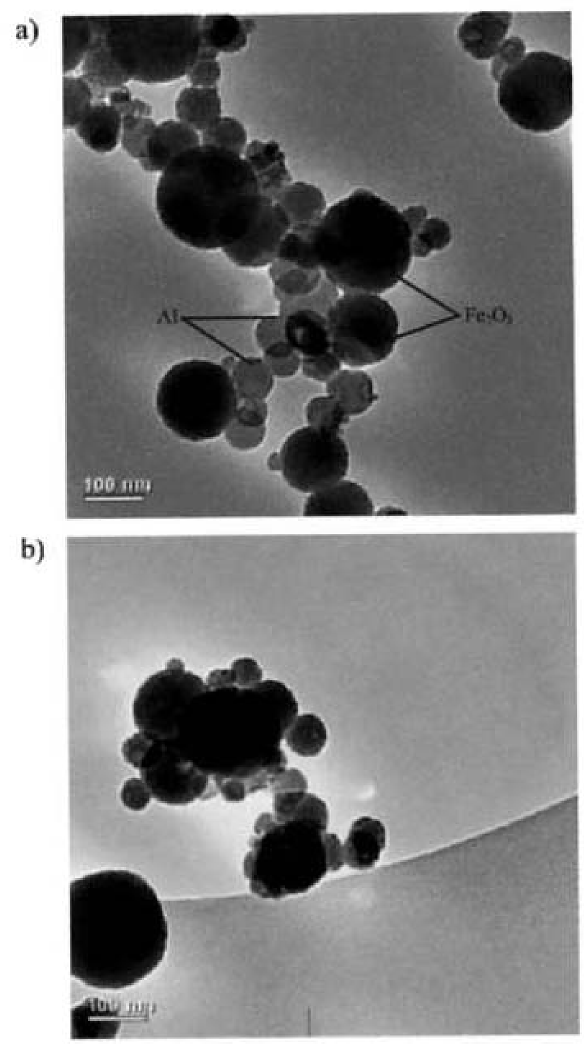
ENCAPSULATION OF Al IN FE_2O_3 MATRIX



Kim and Zachariah (2004)

IMAGES OF NANOCOMPOSITE PARTICLES

TRANSMISION ELECTRON MICROSCOPE



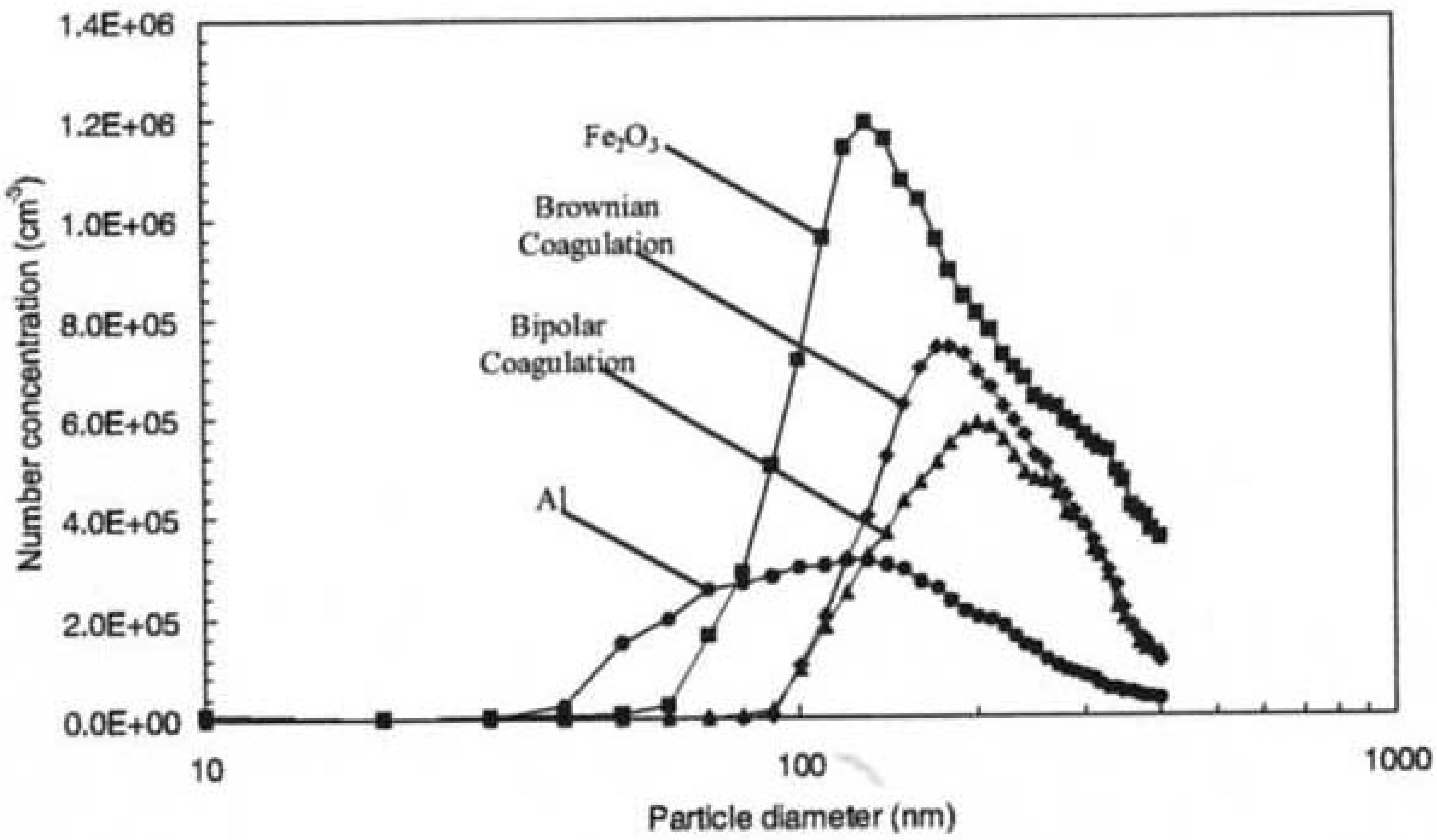
a) Brownian Coagulation

b) Bipolar Coagulation

Kim and Zachariah (2004)

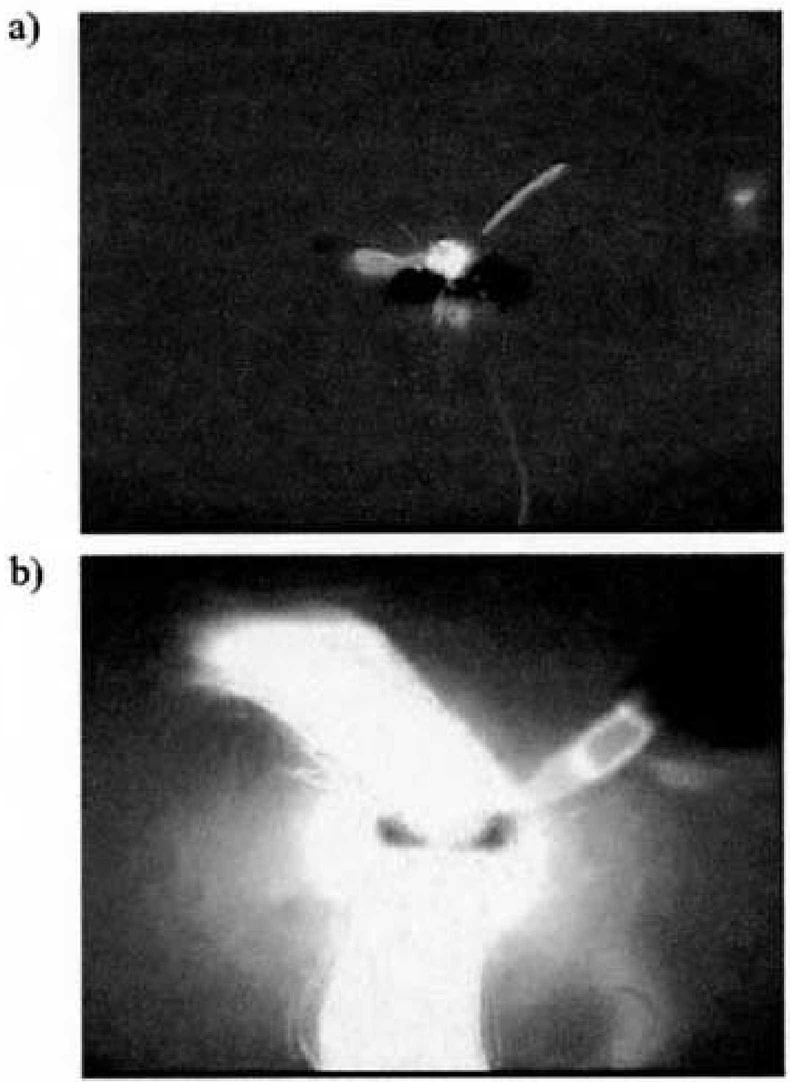
PARTICLE SIZE DISTRIBUTION

DIFFERENTIAL MOBILITY PARTICLE SIZER



Kim and Zachariah (2004)

THERMALLY IGNITED NANOCOMPOSITE PARTICLES



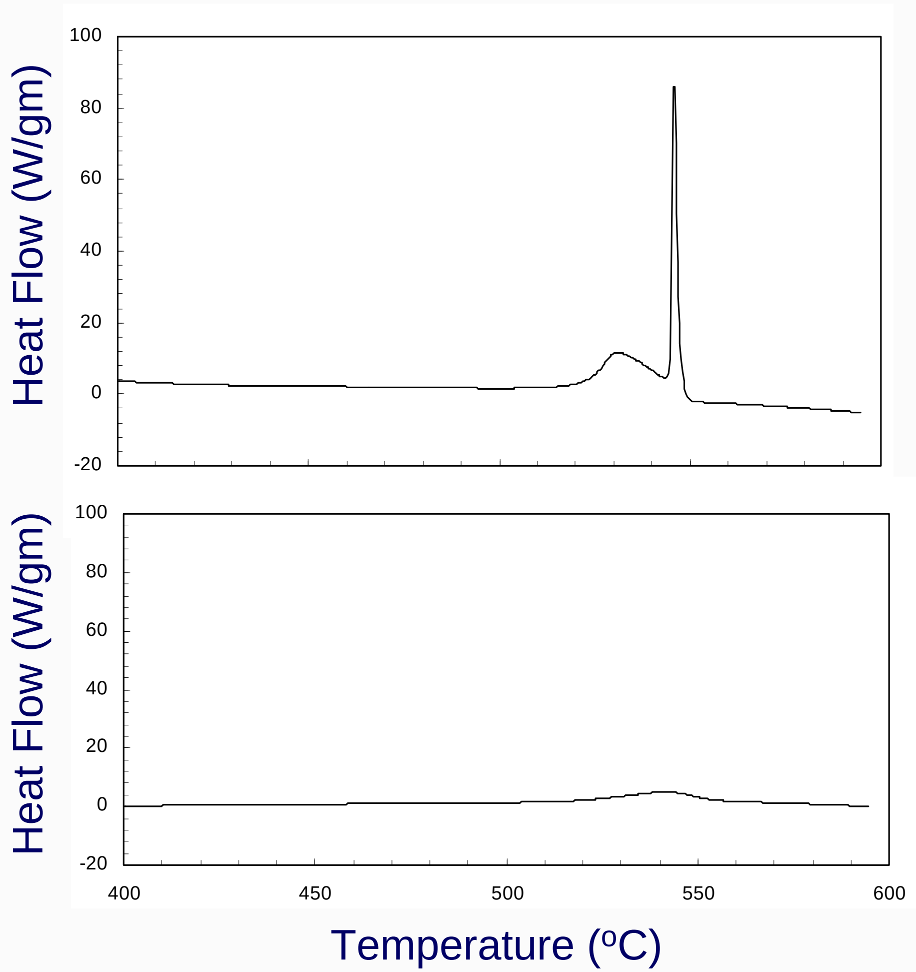
a) Produced by Brownian Coagulation

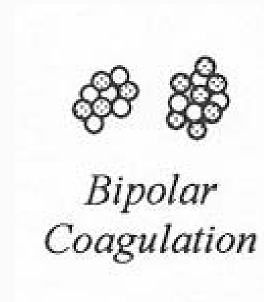
b) Produced by Bipolar Coagulation

Kim and Zachariah (2004)

Reactivity of Al in Fe_2O_3 matrix

M. Zachariah, U. Maryland



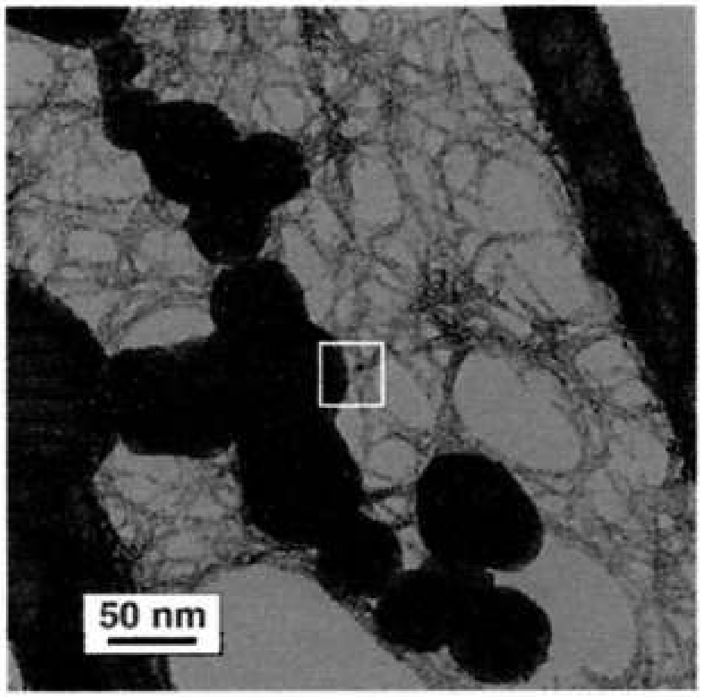


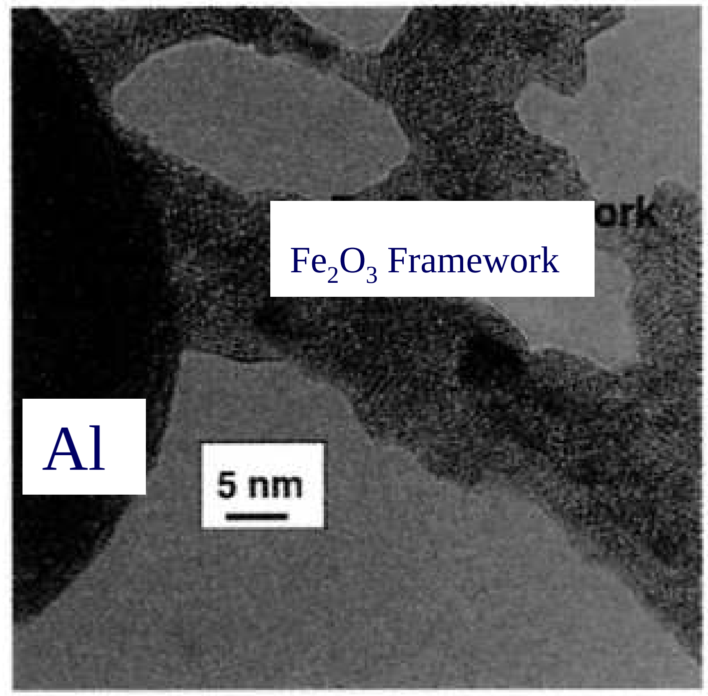
ordered

random

Ordered Nanoparticles Exhibit 10 X Energy Release Rate (Power)

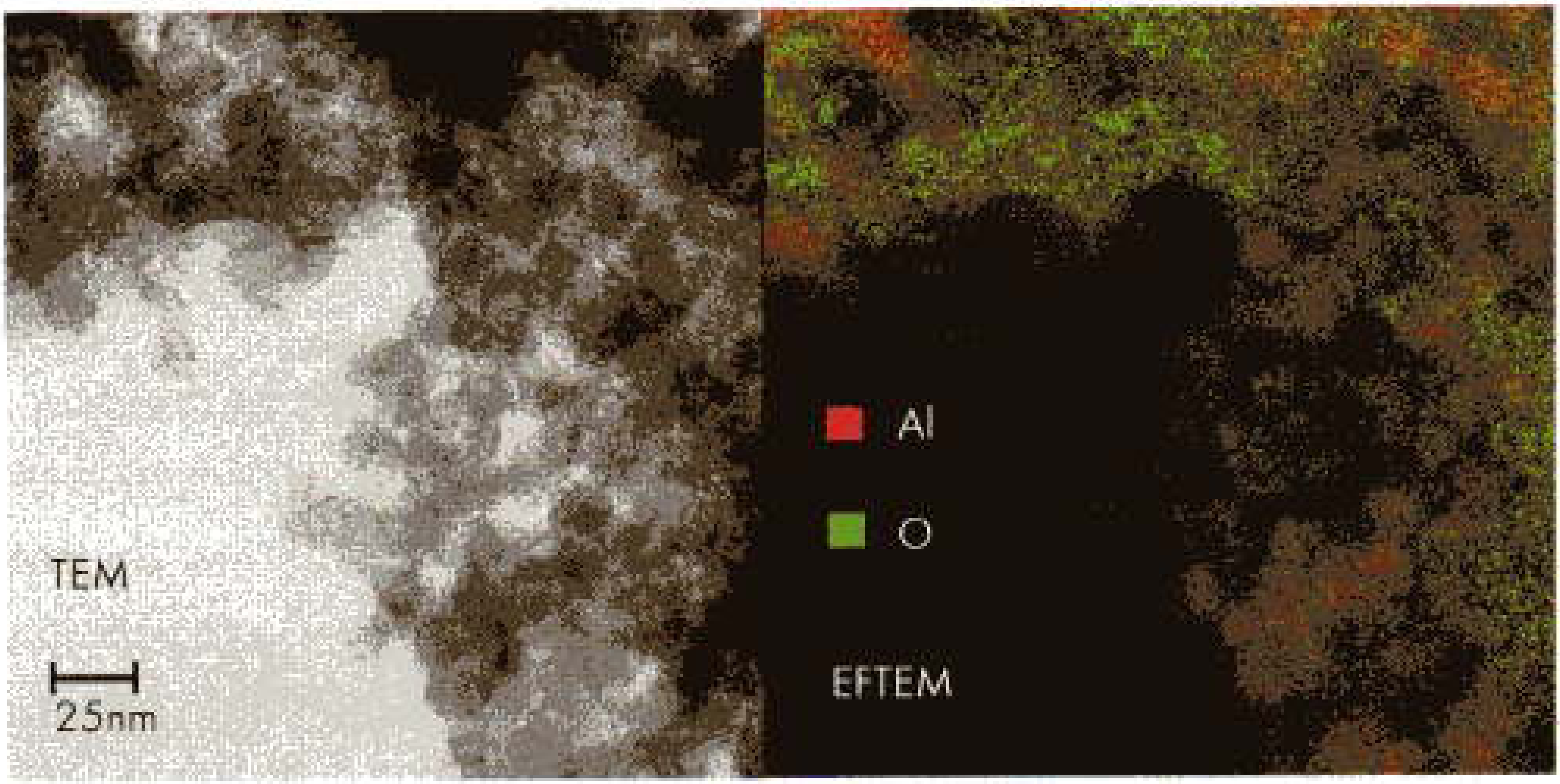
TEM of Sol-Gel Fe_2O_3/UFG Al Nanocomposites





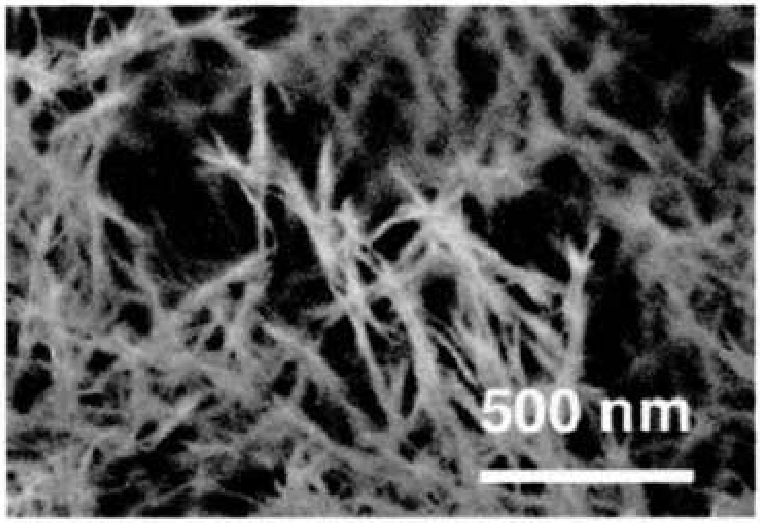
Gash, LLNL

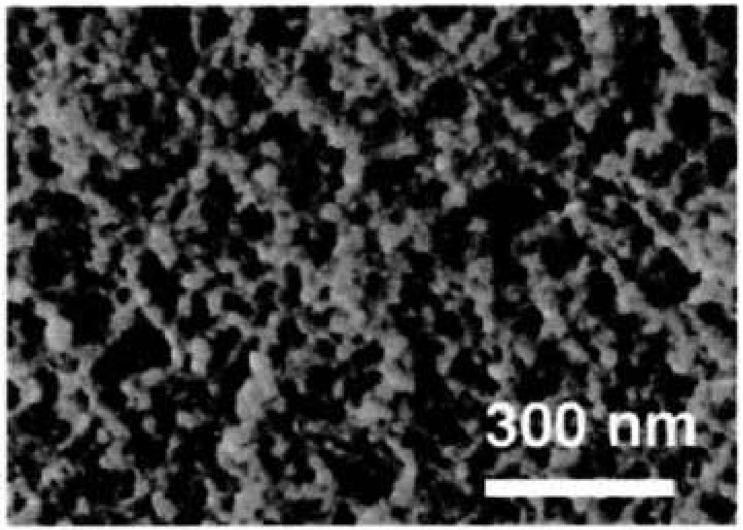
Sol-Gel Fe_2O_3/Al Nanocomposite



LLNL

SEM Images of Sol-Gel Nanomaterials





Iron (ш) Oxide

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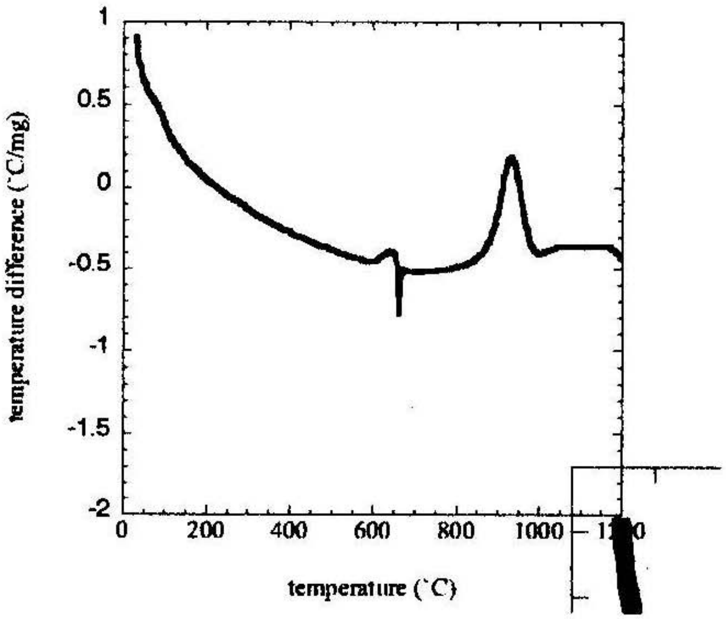
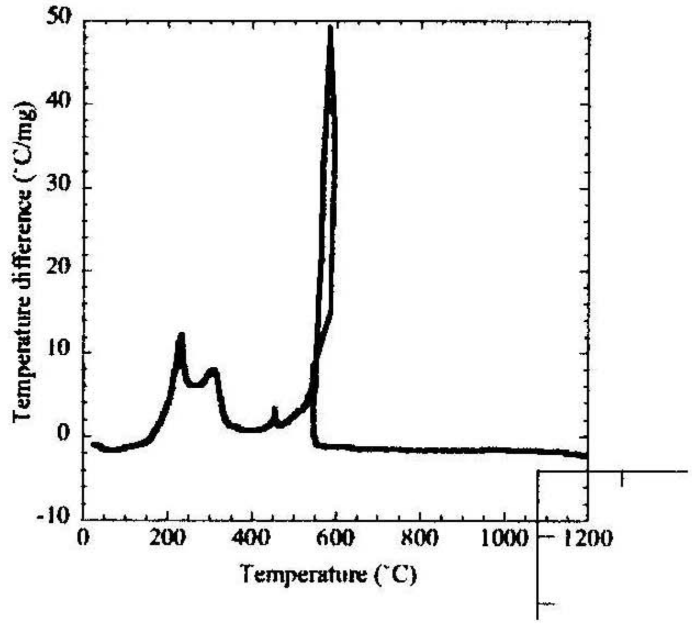
DTA Traces of Fe_2O_3/Al Thermite Materials





Micron-Sized Powder

Sol-Gel Nanostructured Xerogel

Gash, LLNL

Approaches to Nanoenergetics

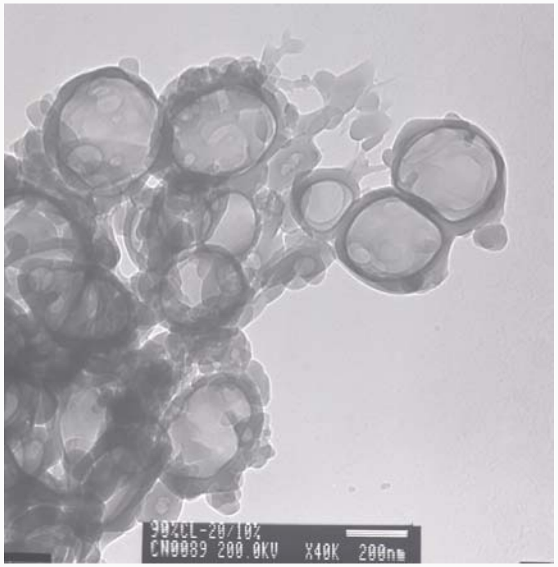
2nd Generation (current efforts)

- Metal oxide / Al sol-gel nanocomposites
  - Pyrotechnics (thermites)
  - High heat and light release
- Organic sol-gel nanocomposites
  - Propellants (explosives)
  - High heat and gas release

Organic Nanocomposites

- Quasi-ordered nanometer-sized inclusions in energetic matrix
    - Cryo-Gel/Sol-Gel processing

CL-20/NC Cryogel



(DURINT - Brill, U. Del.)

MANN, ARO

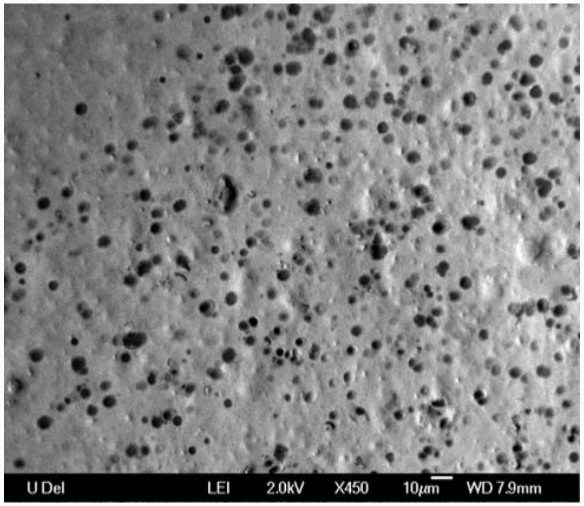
Gelation and Drying

- **Monolithic gel**
  - Polymer, binder
  - Cross-linkers
  - Chain extenders
  - Catalyst and concentration
  - Solvent
  - High explosive
- **Drying procedure**
  - Room temperature evaporation
  - Anti-solvent precipitation and exchange
  - Freeze-drying

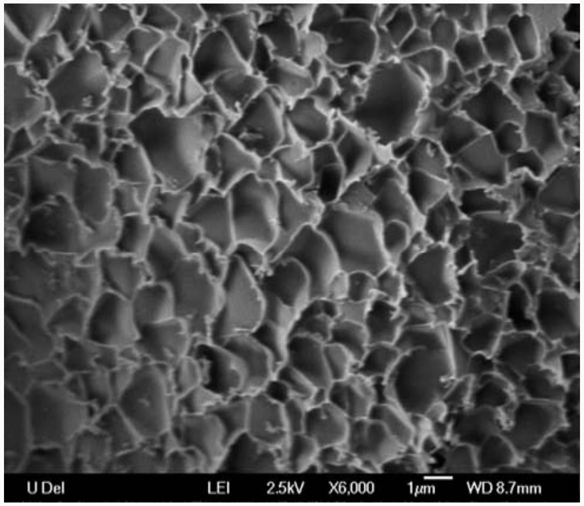
Li and Brill, UoD

Porosity of Cryrogels

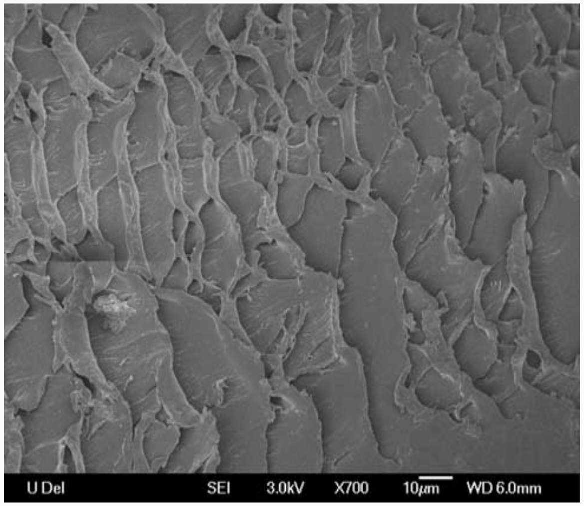
Li and Brill, UoD



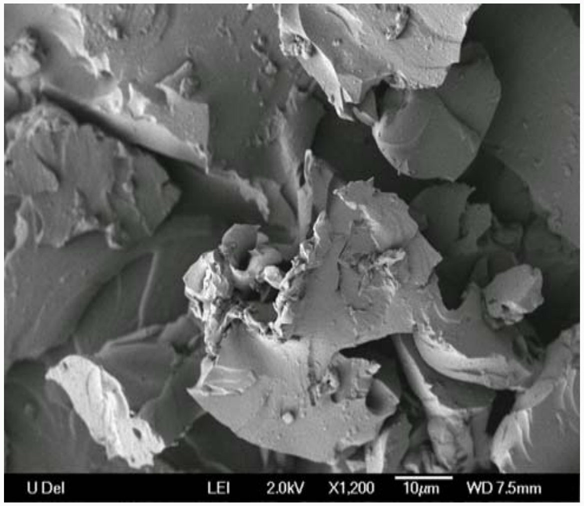
GAP/HDI,90/10



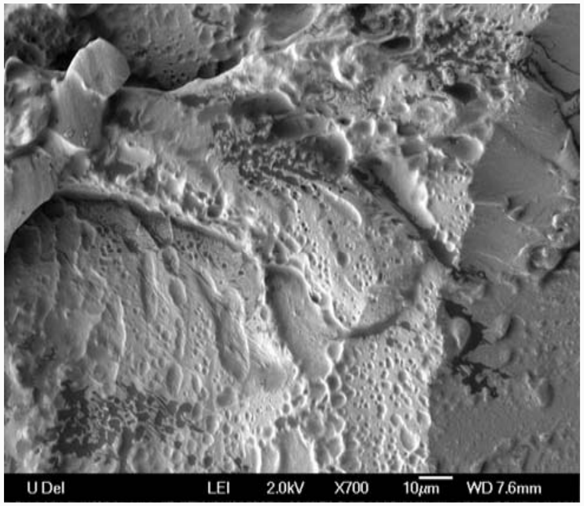
NC/HDI,96/4



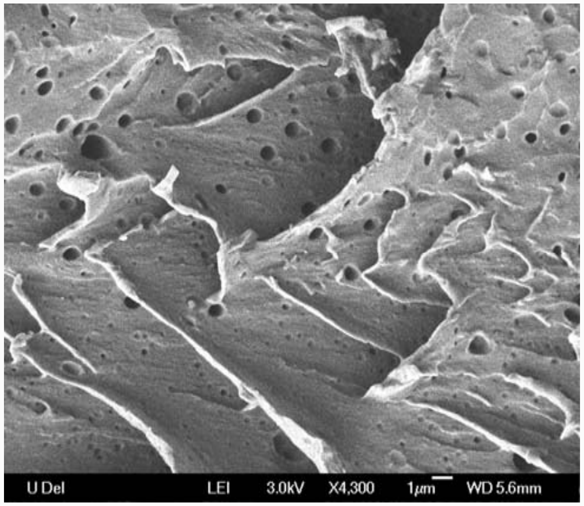
THMNM/HDI,37.46/62.56



GAP/TEGDA, 85/15



NC/GAP/HDI
10/80.62/9.38

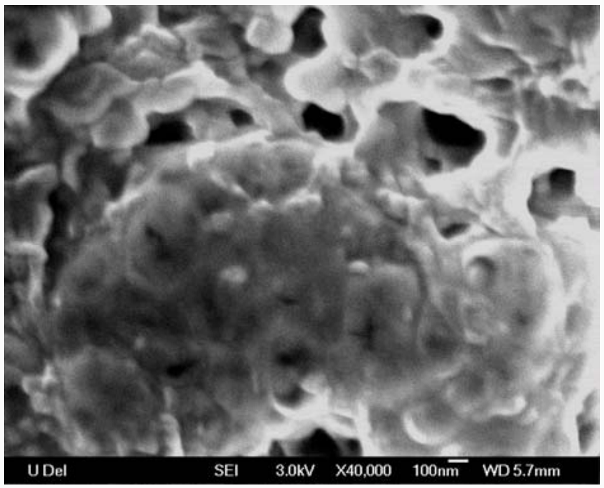


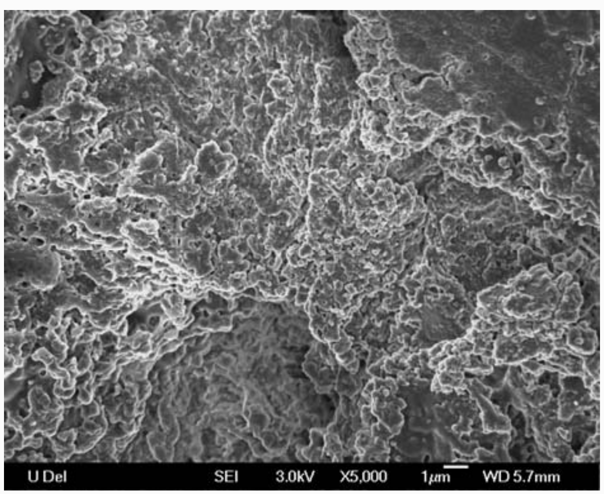
GAP/HDI/THMNM
40/39.20/20.80

SEM of Composite Energetic Materials

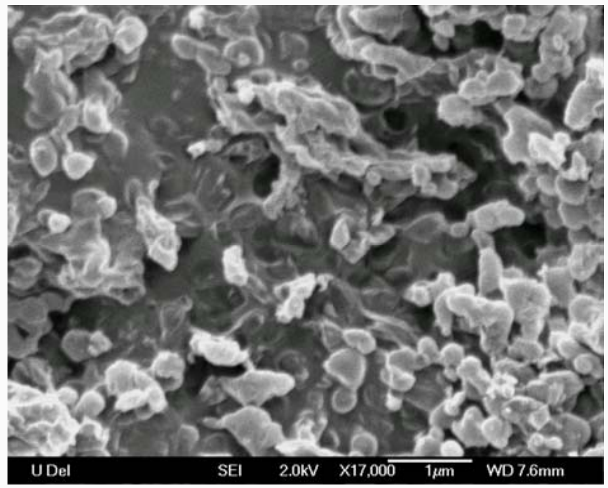
Li and Brill, UoD

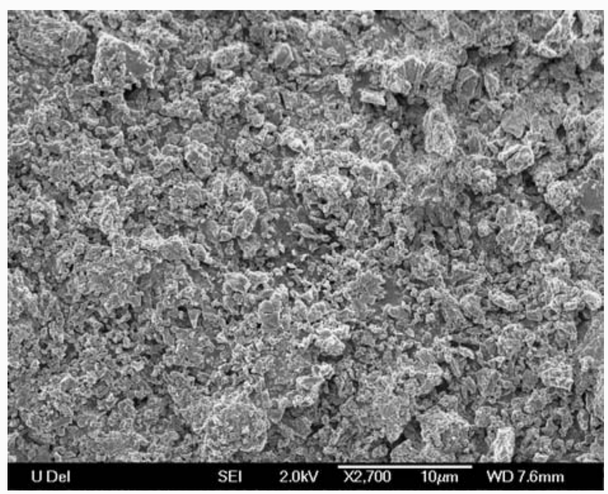
CL-20/GAP/HDI,
85/13.5/1.5



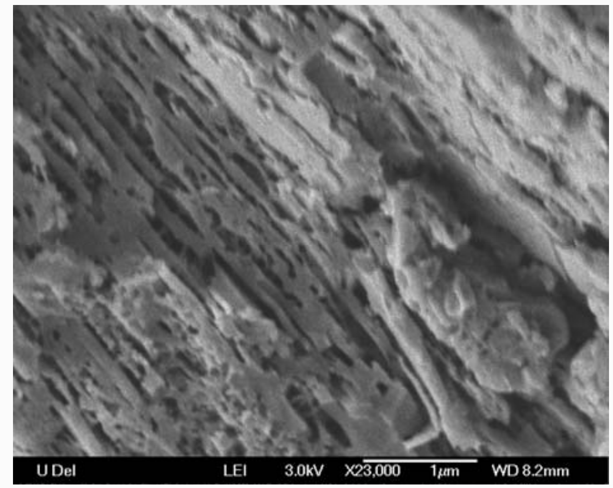


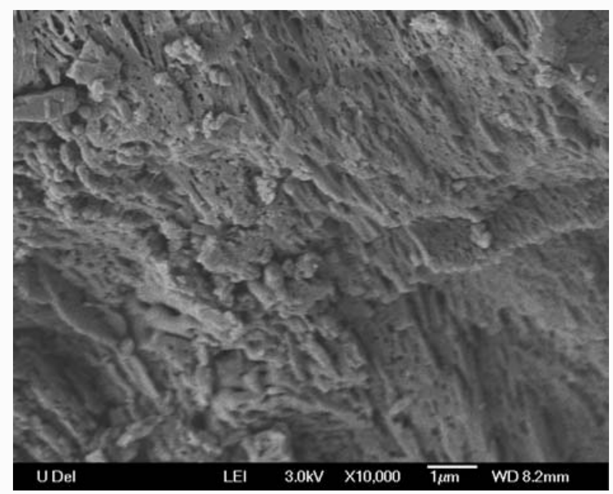
CL-20/NC/HDI,
90/9.6/0.4





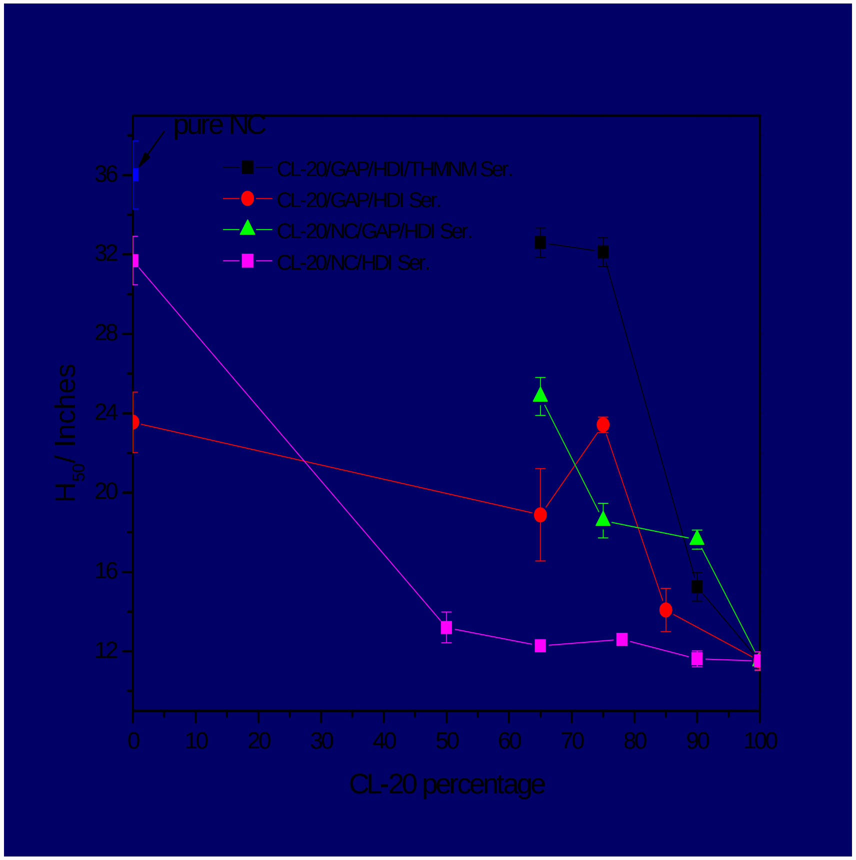
CL-20/THMNM/HDI
90/3.33/6.67



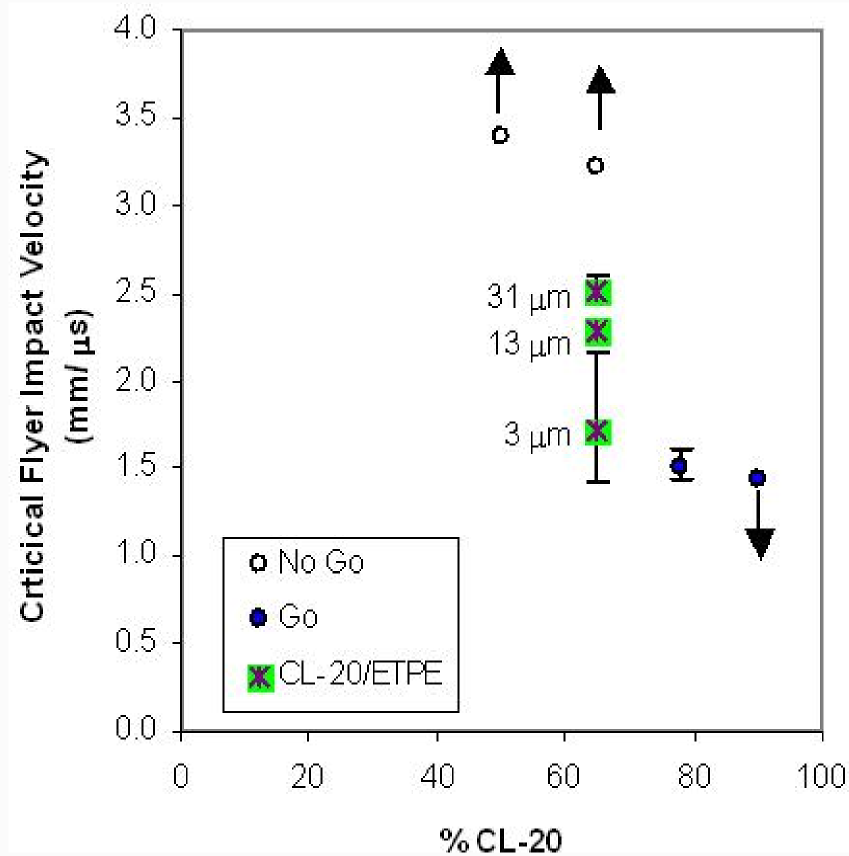


Sensitivity

Impact Sensitivity



Flyer Plate Impact Shock Sensitivity CL-20/NC/HDI



Measurements made by Dr. Brian Roos at ARL on UD samples

Li and Brill, UoD

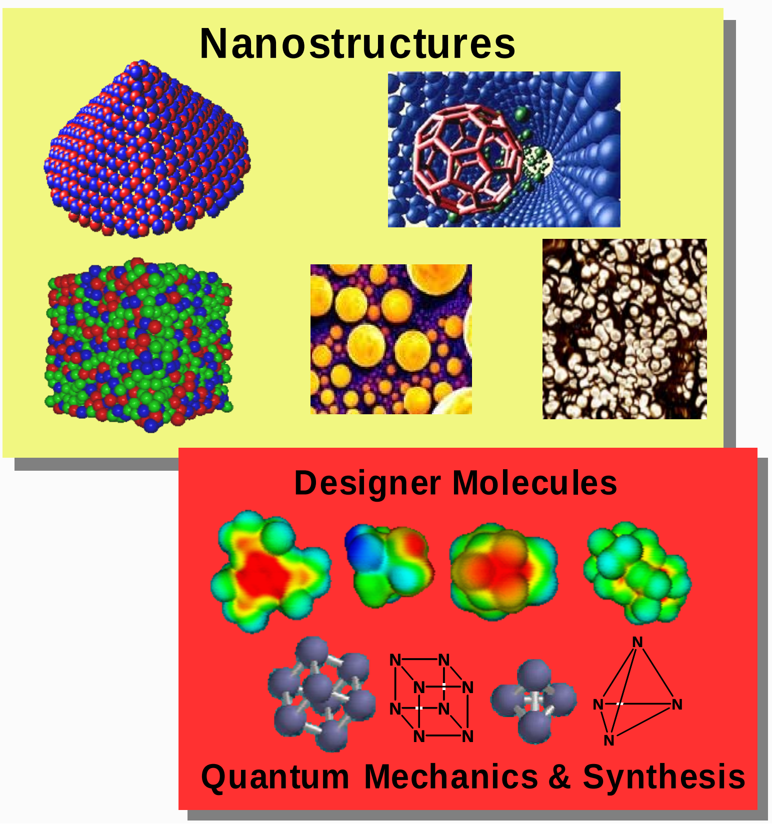
Safety Considerations

- Sol-gel methodology offers advantages in processing (water-like viscocity for casting, ambient temperature gelation and low temperature drying)
- Decreased sensitivity has been observed by shrinking particle size in propellants (more homogeneous mixture, fewer hot spots)
- Reduced sensitivity of explosives observed when produced as nanocomposites (morphology dependent)
- Safety properties need careful evaluation

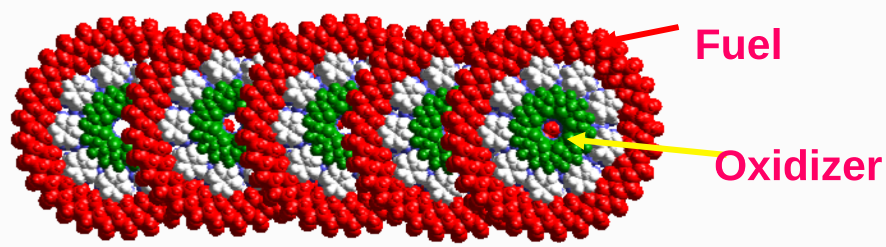
Approaches to Nanoenergetics

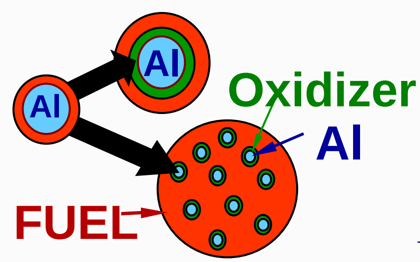
3rd Generation

- 3-dimensional nanoenergetics
    - Structured/ordered
    - Controlled reactivity
    - Improved manufacturability/processing



Nano-Engineered Energetics





MANN, ARO

Nanoscale Energetic Materials

New Ways to Store & Release Chemical Energy

Enable Future Force Propellants & Explosives

- **Increased Energy Storage**
- **Managed Energy Release**
- **Increased Lethality & Range**
- **Reduced Sensitivity**
- **New Weapons Concepts**
- **Increased Storage Lifetime**
- **Green Energetics – Reduced Environmental Impact**

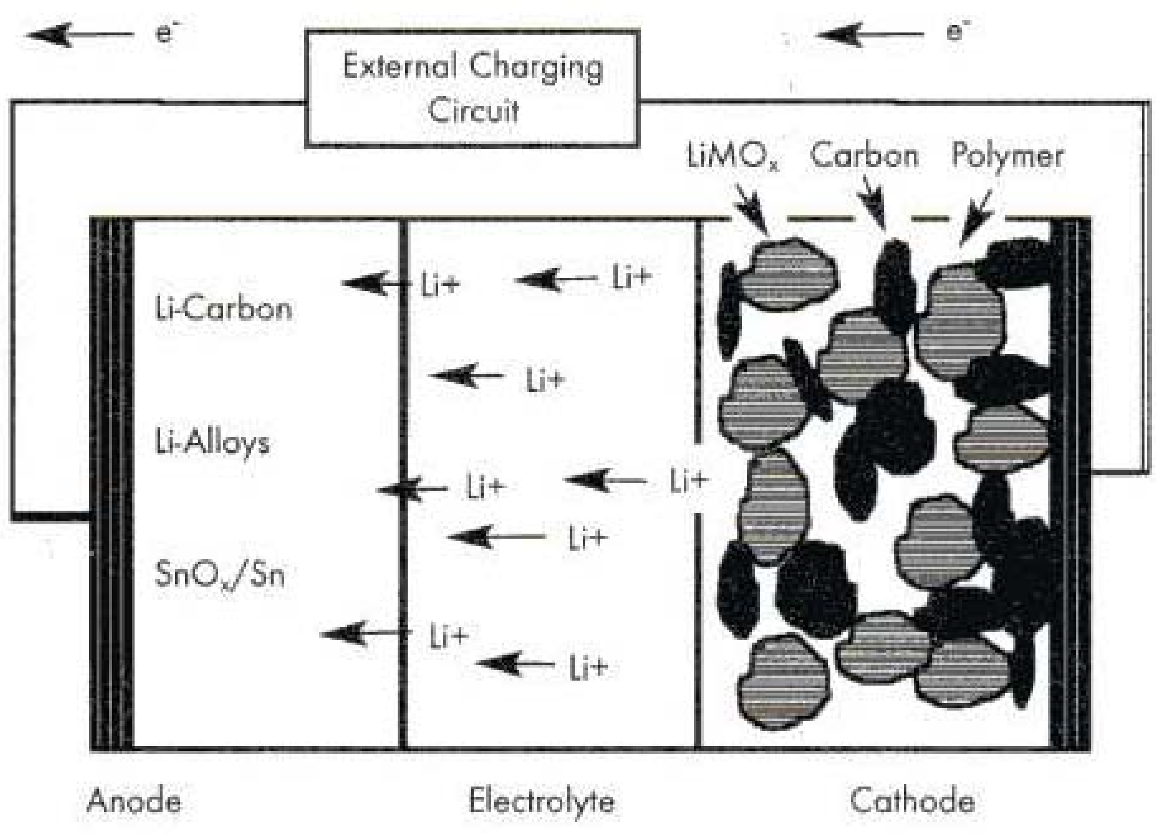
"Built from the Bottom-Up"

MANN, ARO

BATTERIES AND FUEL CELLS

- NANOMATRIALS
  - **ANODE**
  - **CATHODE**
  - **ELECTROLYTE**
  - **CATALYST**
- HYDROGEN STORAGE
  - **CARBON NANOTUBES**
  - **FUNCTIONALIZED NANOTUBES**
  - **NANOSTRUCTURED Mg RELATED MATERIALS**

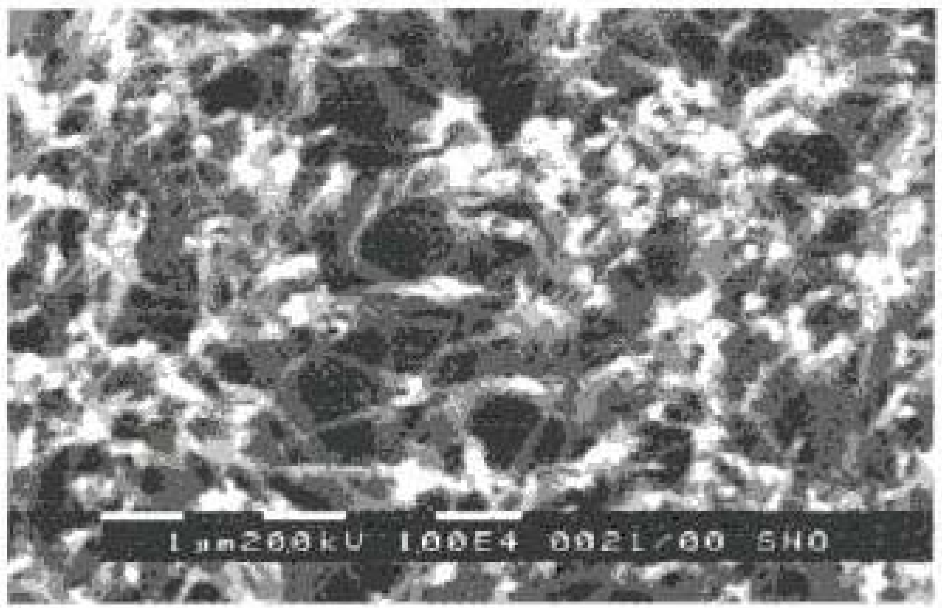
LITHIUM-ION CELL



CARLIN, ONR

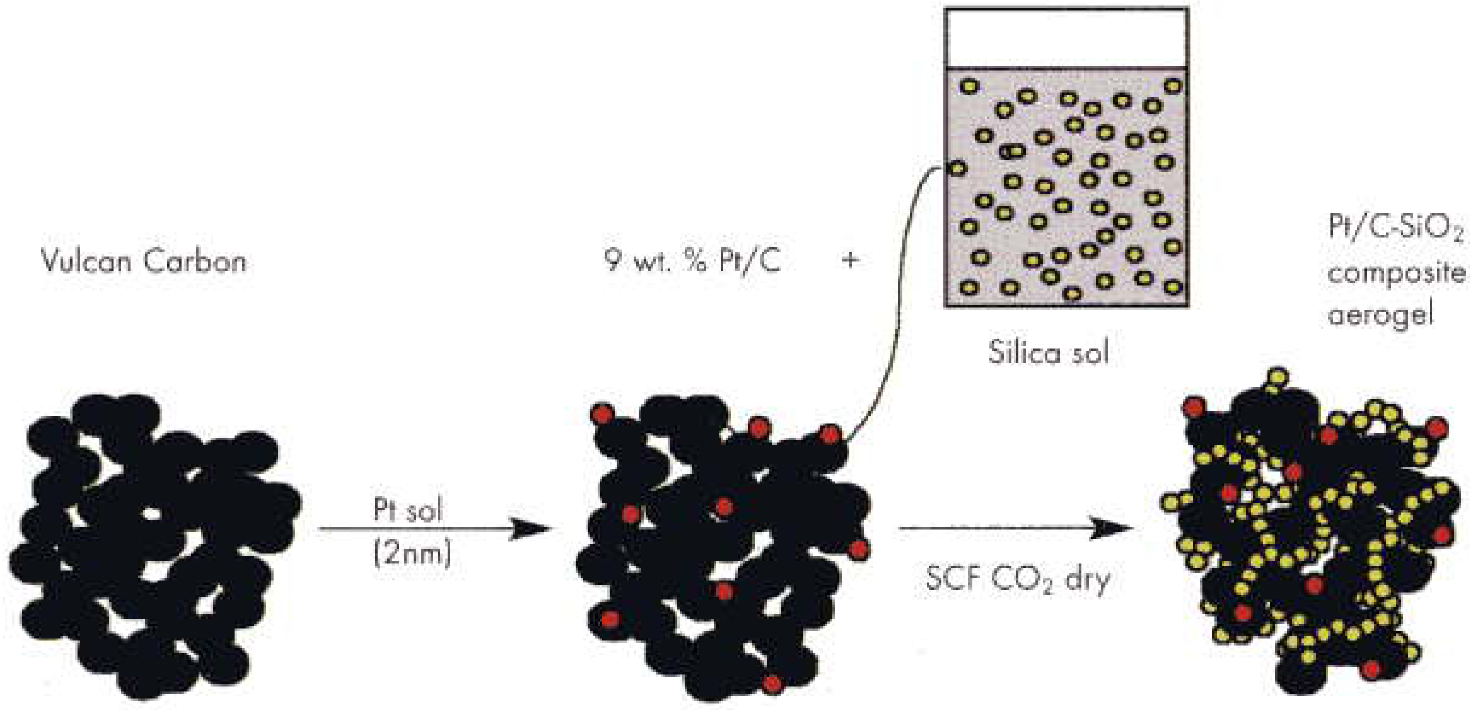
NANOMATERIAL ANODES

SnO_2 Nanofibers



CARLIN, ONR

NANOARCHITECURED Pt/C-SiO_2 CATALYST

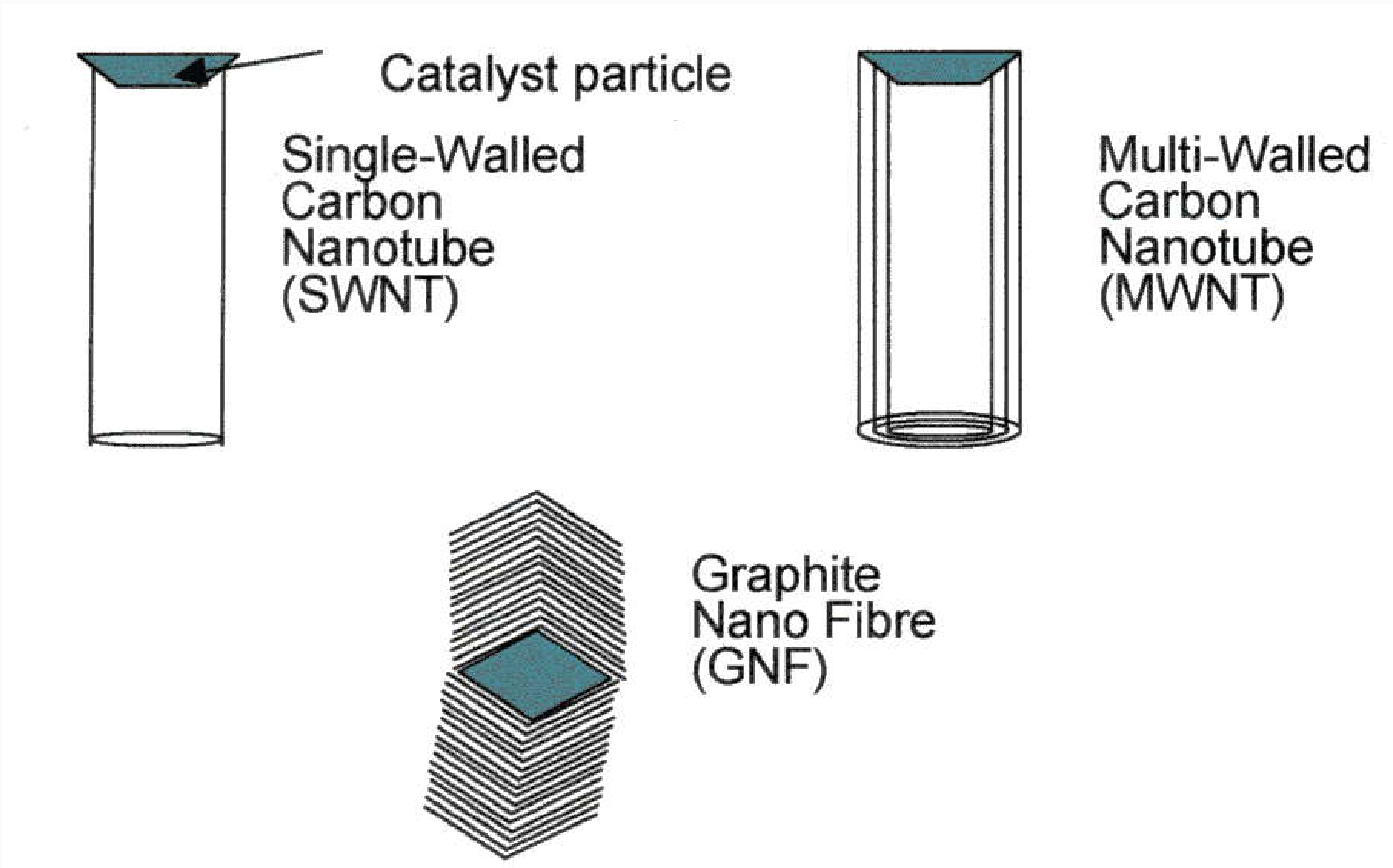


CARLIN, ONR

BATTERIES AND FUEL CELLS

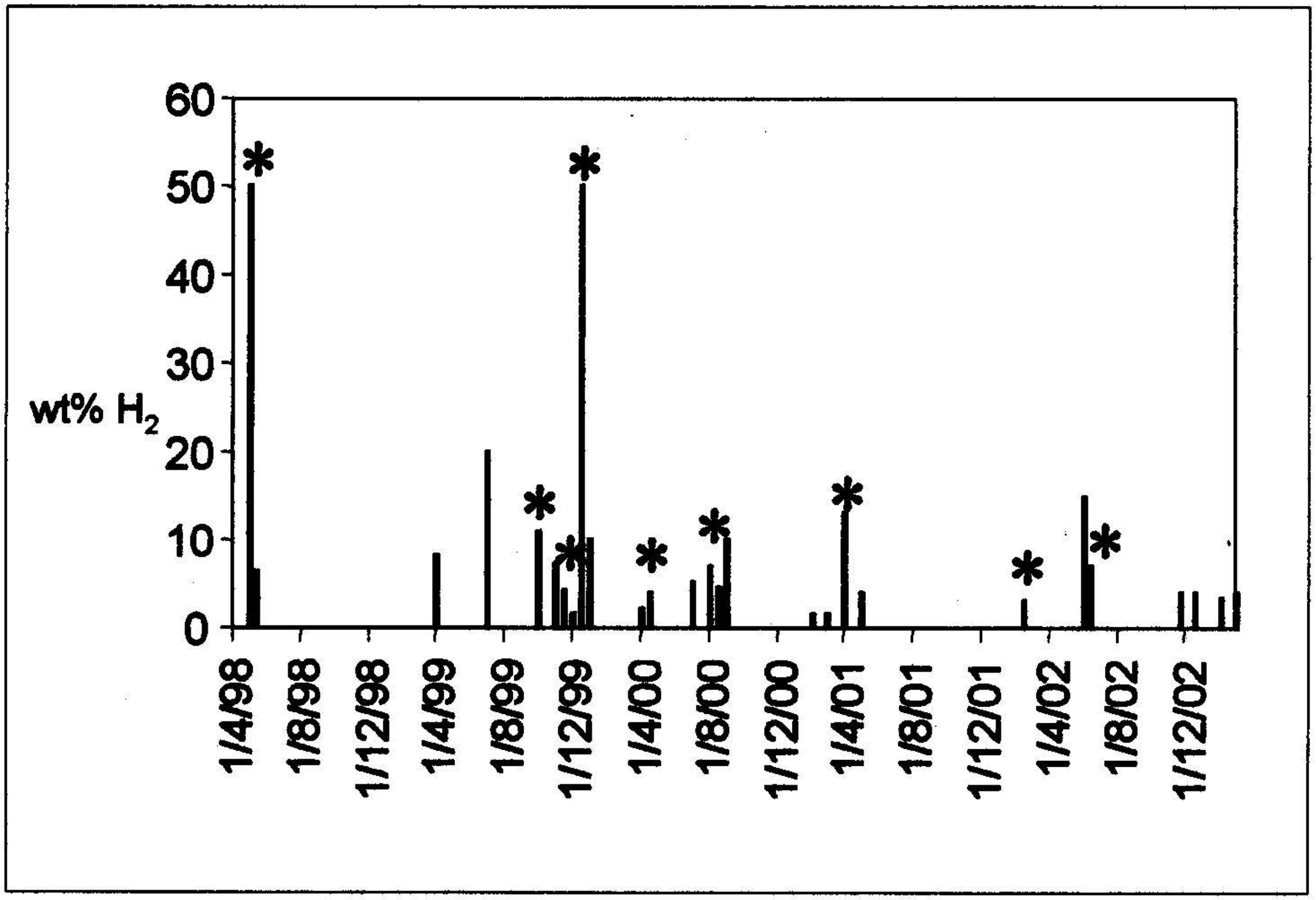
- NANOMATRIALS
  - **ANODE**
  - **CATHODE**
  - **ELECTROLYTE**
  - **CATALYST**
- HYDROGEN STORAGE
  - **CARBON NANOTUBES**
  - **NANOSTRUCTURED Mg RELATED MATERIALS**
  - **FUNCTIONALIZED NANOTUBES**

DIFFERENT TYPES OF NANOCARBON



SHATWELL, QinetiQ

HYDROGEN ADSORPTION ON NANOCARBONS



SHATWELL, QinetiQ

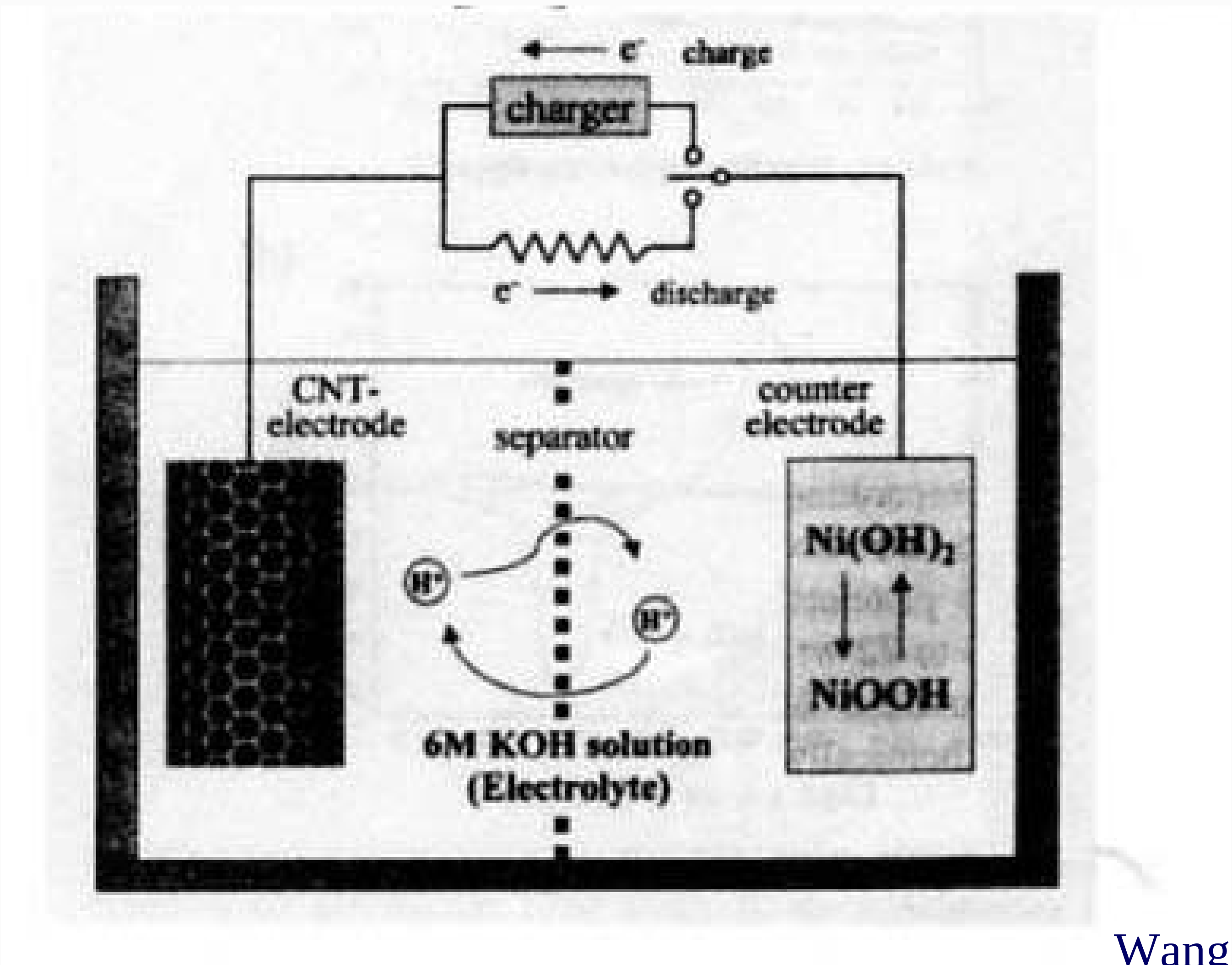
QinetiQ GRAPHIT NANO FIBRE

SHATWELL, QinetiQ

FUNCTIONALIZED NANOTUBES

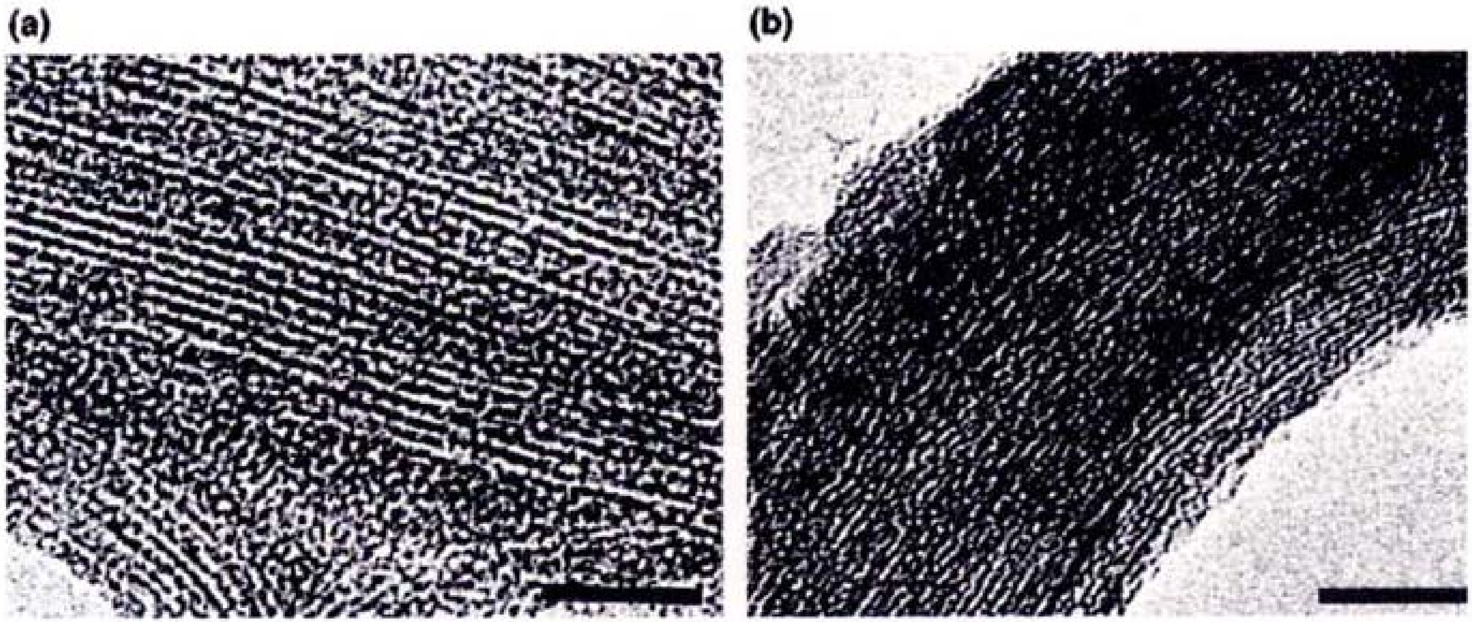
- Hydrogen adsorption by
  - Chemical reactions
  - Electrochemical technique
    - With and without catalyst

Set-Up for Electrochemical Functionalization with Hydrogen



Wang, NJIT

TEM Images from SWNT Bundles



Pristine Sheet

Electromechanically Functionalized Sheet

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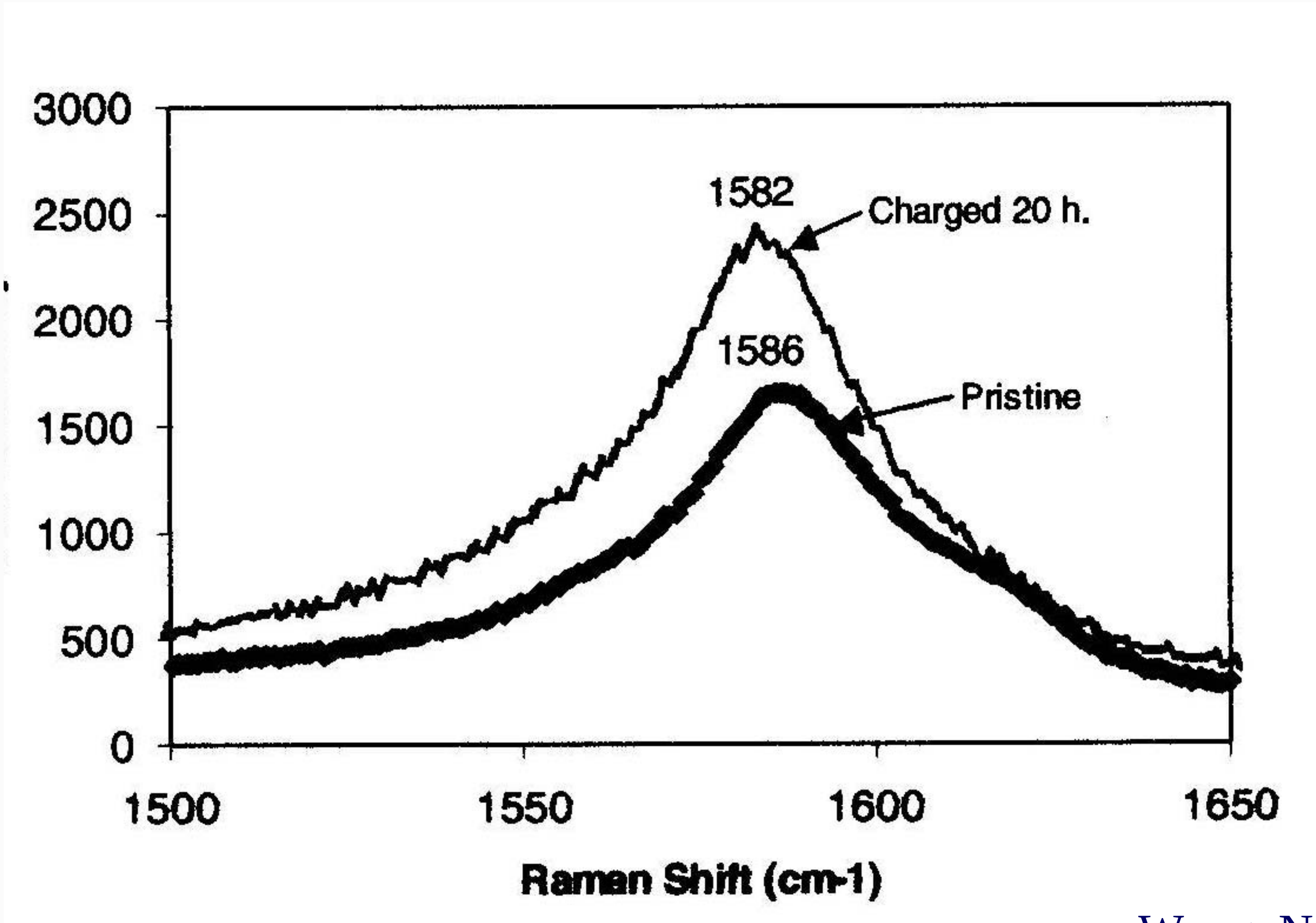
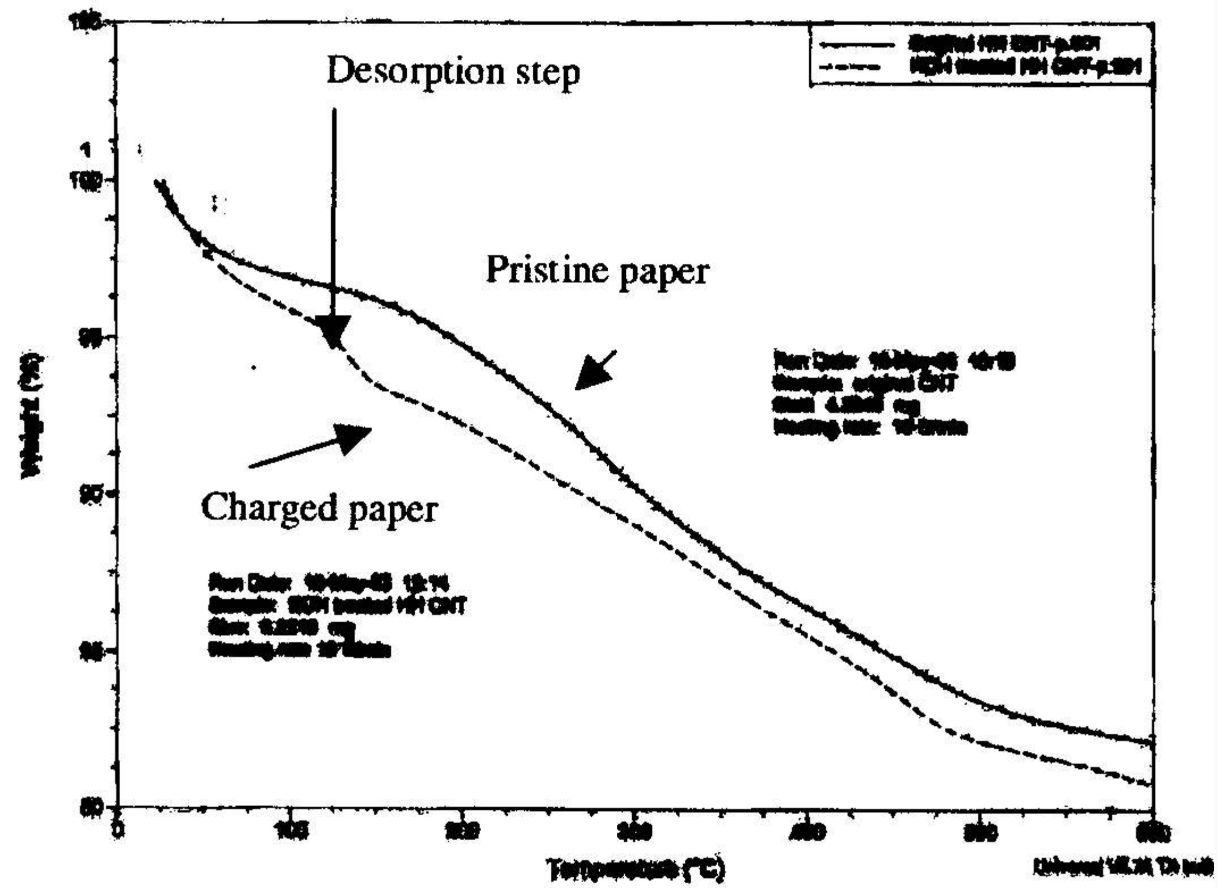
Raman Lines for Pristine and Electrochemically Charged Nanopaper



Wang, NJIT

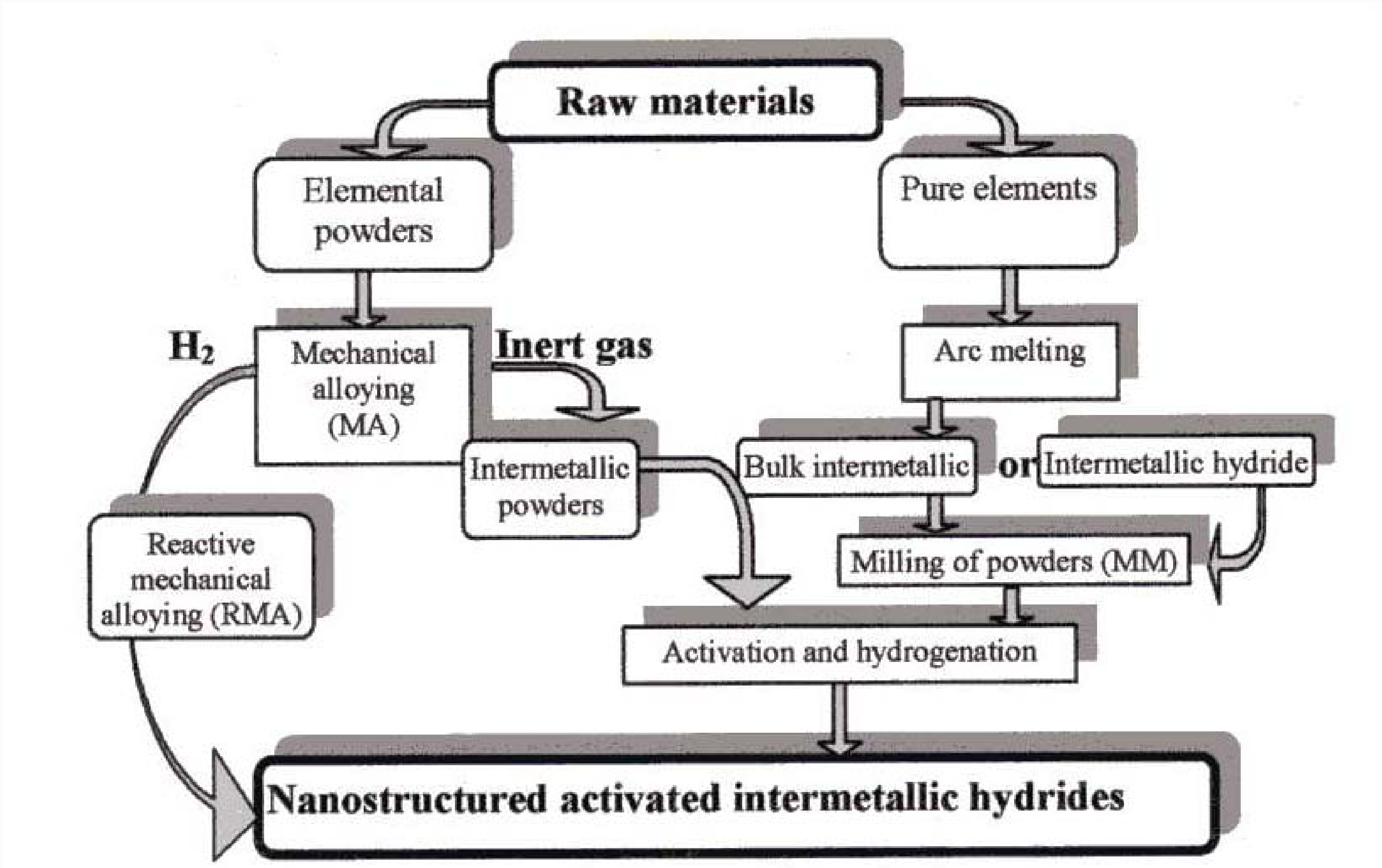
TGA Data for Mg Coated and Pristine Nanopaper



Adsorbed hydrogen level: 2.0 weight percent (without catalyst)
Enhanced by electrochemically deposited Mg coating

Wang, NJIT

POSSIBLE ROUTES OF MANUFACTURING NANOSTRUCTURED INTERMETALLICS



BYSTRZYCKI, MUT WARSAW

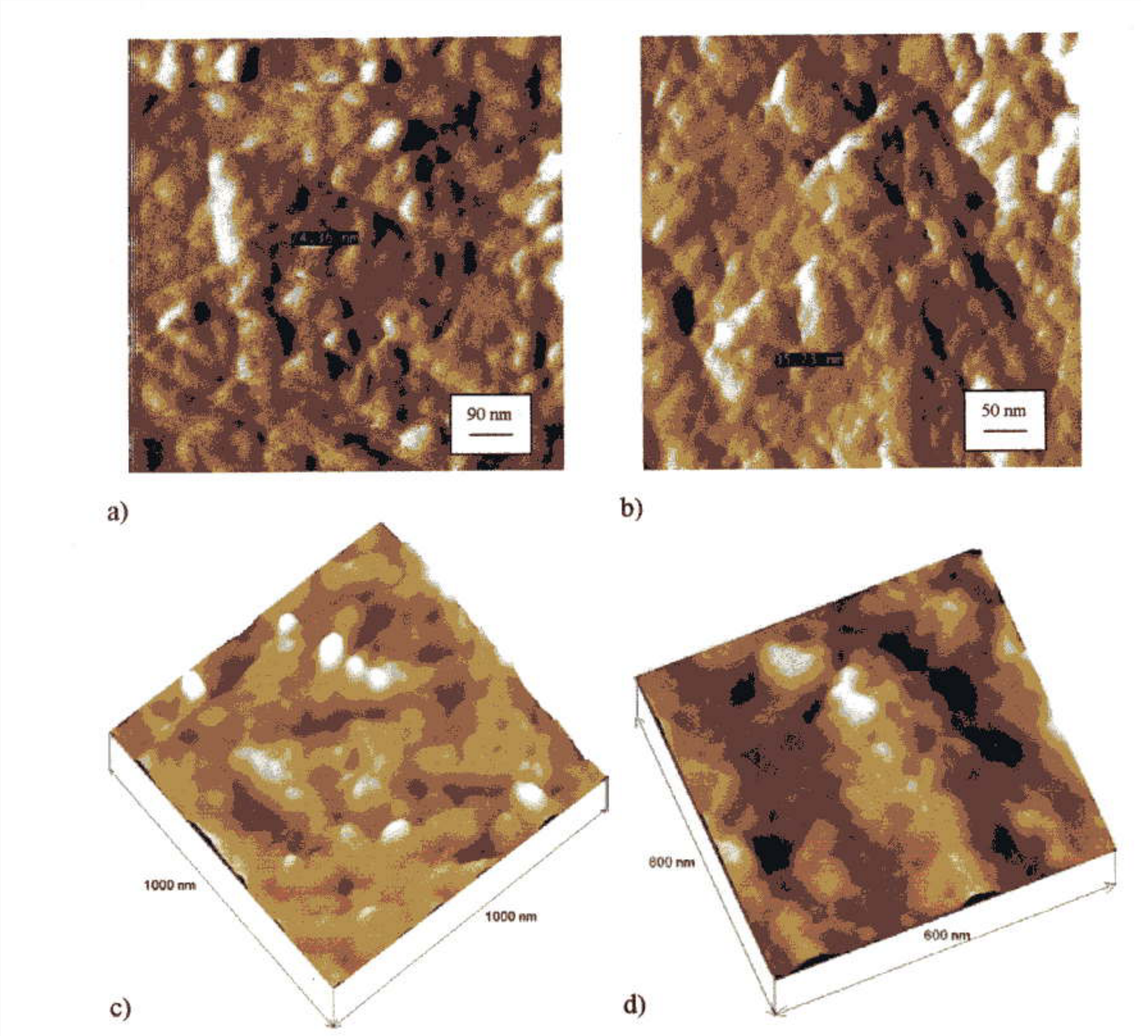
NANOCRYSTALLINE MECHANICALLY ALLOYED (MA) HYDROGEN STORAGE INTERMETALLICS

Intermetallic Compound (alloy)	**Compound forms during MA**	**H sorption/desorption properties**		**Ref.**
		Maximum H absorbed/desorbed [wt.%]	*Kinetics*	
Mg_2Ni	Yes (~10 nm) (20-30 nm)	~3.2/?(300°C) ~2.4/?(200°C) ~0.8/?(150°C)	***No Ac*** tFsAb(↓)(300°C) T_{Ab}(↓)	5,39 58
Mg_2Ni(+trace Ni)	Yes (<20 nm)	3.75/3.2(300°C) 2.8/1.5(200°C) 0.7/small(30°C)	***No Ac***	23
$(Mg_{1.8}Zr_{0.2})Ni$	Partly (amorph.+nano Mg_2Ni)	3.0/2.0(200°C) 2.3/?(30°C)	***No Ac***	23
$Mg_2(Ni_{1.9}M_{0.1})$ *	Amorphous	1.7-2.2/~0 (100°C)	?	27
"MgNi"	Amorphous	1.72/**(200°C)	-	28
$Mg_{17}Al_{12}$ in Mg-Al	Yes	3.9(400°C)	Yes	3

* Essentially "MgNi" alloy; Milled with Ni in 1:1 ratio; M=Ni, Ca, La, Y, Al, Si, Cu, Mn [27].

** Decomposes into $Mg_2NiH_4+MgNi_2$ during measurements of PCT curve [28].

NANOSTRUCTURES ON NANOCRYSTALLINE Mg_2Ni POWDERS



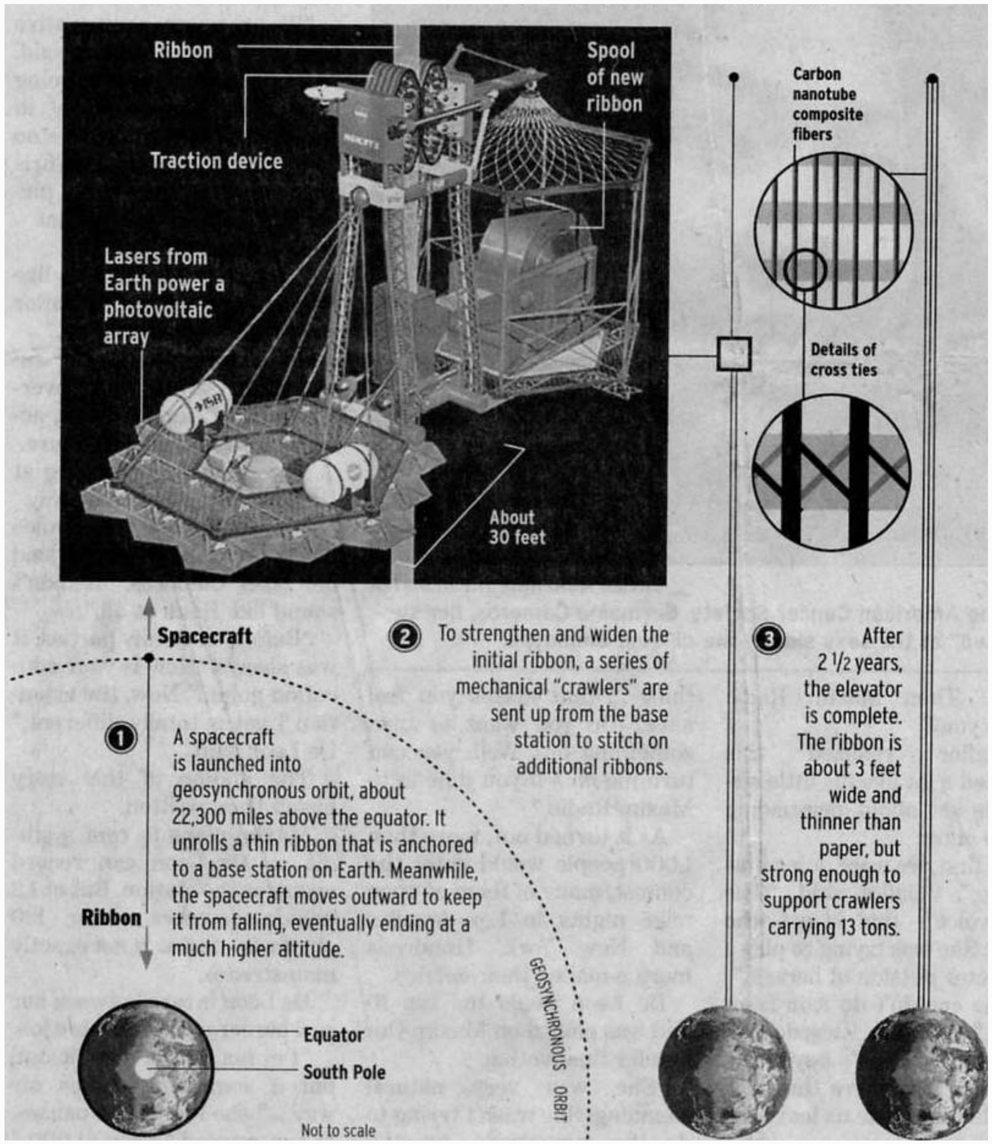
BYSTRZYCKI, MUT WARSAW

CONCLUSION

- NANOMATERIALS HAVE HIGH POTENTIAL FOR ENERGETICS AND POWER GENERATION
- GROUNDBREAKING WORK HAS SHOWN FIRST SUCCESSES
- SCIENCE AT NANOSCALE HAS TO BE ADVANCED FOR UNDERSTANDING, CONTROL, AND FABRICATION OF COMPLEX STRUCTURES

GOING UP

62000-mile Elevator for Space Cargo



NASA

NASA SPACE ELEVATOR